



07-07-07

A

Practitioner's Docket No. 1060A**PATENT****Preliminary Classification:**

Proposed Class: 429

Subclass: 224

**NOTE:** *"All applicants are requested to include a preliminary classification on newly filed patent applications. The preliminary classification, preferably class and subclass designations, should be identified in the upper right-hand corner of the letter of transmittal accompanying the application papers, for example 'Proposed Class 2, subclass 129.'" M.P.E.P. § 601, 7th ed.*

1060A U.S. PTO  
09/610821  
07/06/00**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

**Box Patent Application**  
**Assistant Commissioner for Patents**  
**Washington, D.C. 20231**

**NEW APPLICATION TRANSMITTAL**

Transmitted herewith for filing is the patent application of

**Inventor(s):** Terrell Neils Andersen, Samuel Faust Burkhardt, Wilmont Frederick Howard, Jr., Richard F. Wohletz, Vahid Kazerooni, Mohammad Reza Moumenzadeh and Amy Wren Unsell

**WARNING:** 37 C.F.R. § 1.41(a)(1) points out:

*"(a) A patent is applied for in the name or names of the actual inventor or inventors.*

*"(1) The inventorship of a nonprovisional application is that inventorship set forth in the oath or declaration as prescribed by § 1.63, except as provided for in § 1.53(d)(4) and § 1.63(d). If an oath or declaration as prescribed by § 1.63 is not filed during the pendency of a nonprovisional application, the inventorship is that inventorship set forth in the application papers filed pursuant to § 1.53(b), unless a petition under this paragraph accompanied by the fee set forth in § 1.17(i) is filed supplying or changing the name or names of the inventor or inventors."*

**For (title):**

HIGH DISCHARGE CAPACITY ELECTROLYTIC MANGANESE DIOXIDE  
AND METHODS OF PRODUCING THE SAME

**CERTIFICATION UNDER 37 C.F.R. § 1.10\****(Express Mail label number is mandatory.)**(Express Mail certification is optional.)*

I hereby certify that this New Application Transmittal and the documents referred to as attached therein are being deposited with the United States Postal Service on this date July 6, 2000 in an envelope as "Express Mail Post Office to Addressee," mailing Label Number EL 495 102 459 US, addressed to the: Assistant Commissioner for Patents, Washington, D.C. 20231.

Dana M. Coots*(type or print name of person mailing paper)*Dana M. Coots**Signature of person mailing paper**

**WARNING:** Certificate of mailing (first class) or facsimile transmission procedures of 37 C.F.R. § 1.8 cannot be used to obtain a date of mailing or transmission for this correspondence.

**\*WARNING:** Each paper or fee filed by "Express Mail" **must** have the number of the "Express Mail" mailing label placed thereon prior to mailing. 37 C.F.R. § 1.10(b).

"Since the filing of correspondence under § 1.10 without the Express Mail mailing label thereon is an oversight that can be avoided by the exercise of reasonable care, requests for waiver of this requirement will **not** be granted on petition." Notice of Oct. 24, 1996, 60 Fed. Reg. 56,439, at 56,442.

## 1. Type of Application

This new application is for a(n)

(check one applicable item below)

- Original (nonprovisional)
- Design
- Plant

**WARNING:** *Do not use this transmittal for a completion in the U.S. of an International Application under 35 U.S.C. § 371(c)(4), unless the International Application is being filed as a divisional, continuation or continuation-in-part application.*

**WARNING:** *Do not use this transmittal for the filing of a provisional application.*

**NOTE:** *If one of the following 3 items apply, then complete and attach ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF A PRIOR U.S. APPLICATION CLAIMED and a NOTIFICATION IN PARENT APPLICATION OF THE FILING OF THIS CONTINUATION APPLICATION.*

- Divisional.
- Continuation.
- Continuation-in-part (C-I-P).

## 2. Benefit of Prior U.S. Application(s) (35 U.S.C. §§ 119(e), 120, or 121)

**NOTE:** *A nonprovisional application may claim an invention disclosed in one or more prior filed copending nonprovisional applications or copending international applications designating the United States of America. In order for a nonprovisional application to claim the benefit of a prior filed copending nonprovisional application or copending international application designating the United States of America, each prior application must name as an inventor at least one inventor named in the later filed nonprovisional application and disclose the named inventor's invention claimed in at least one claim of the later filed nonprovisional application in the manner provided by the first paragraph of 35 U.S.C. § 112. Each prior application must also be:*

- (i) An international application entitled to a filing date in accordance with PCT Article 11 and designating the United States of America; or*
- (ii) Complete as set forth in § 1.51(b); or*
- (iii) Entitled to a filing date as set forth in § 1.53(b) or § 1.53(d) and include the basic filing fee set forth in § 1.16; or*
- (iv) Entitled to a filing date as set forth in § 1.53(b) and have paid therein the processing and retention fee set forth in § 1.21(l) within the time period set forth in § 1.53(f).*

*37 C.F.R. § 1.78(a)(1).*

**NOTE:** *If the new application being transmitted is a divisional, continuation or a continuation-in-part of a parent case, or where the parent case is an International Application which designated the U.S., or benefit of a prior provisional application is claimed, then check the following item and complete and attach ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.*

**WARNING:** *If an application claims the benefit of the filing date of an earlier filed application under 35 U.S.C. §§ 120, 121 or 365(c), the 20-year term of that application will be based upon the filing date of the earliest U.S. application that the application makes reference to under 35 U.S.C. §§ 120, 121 or 365(c). (35 U.S.C. § 154(a)(2) does not take into account, for the determination of the patent term, any application on which priority is claimed under 35 U.S.C. §§ 119, 365(a) or 365(b).) For a c-i-p application, applicant should review whether any claim in the patent that will issue is supported by an earlier application and, if not, the applicant should consider canceling the reference to the earlier filed application. The term of a patent is not based on a claim-by-claim approach. See Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,205.*

**WARNING:** When the last day of pendency of a provisional application falls on a Saturday, Sunday, or Federal holiday within the District of Columbia, any nonprovisional application claiming benefit of the provisional application must be filed prior to the Saturday, Sunday, or Federal holiday within the District of Columbia. See 37 C.F.R. § 1.78(a)(3).

The new application being transmitted claims the benefit of prior U.S. application(s). Enclosed are ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

### 3. Papers Enclosed

A. Required for filing date under 37 C.F.R. § 1.53(b) (Regular) or 37 C.F.R. § 1.153 (Design) Application

38 Pages of specification

6 Pages of claims

11 Sheets of drawing

**WARNING:** DO NOT submit original drawings. A high quality copy of the drawings should be supplied when filing a patent application. The drawings that are submitted to the Office must be on strong, white, smooth, and non-shiny paper and meet the standards according to § 1.84. If corrections to the drawings are necessary, they should be made to the original drawing and a high-quality copy of the corrected original drawing then submitted to the Office. Only one copy is required or desired. For comments on proposed then-new 37 C.F.R. § 1.84, see Notice of March 9, 1988 (1990 O.G. 57-62).

**NOTE:** "Identifying indicia, if provided, should include the application number or the title of the invention, inventor's name, docket number (if any), and the name and telephone number of a person to call if the Office is unable to match the drawings to the proper application. This information should be placed on the back of each sheet of drawing a minimum distance of 1.5 cm. (5/8 inch) down from the top of the page . . ." 37 C.F.R. § 1.84(c)).

(complete the following, if applicable)

The enclosed drawing(s) are photograph(s), and there is also attached a "PETITION TO ACCEPT PHOTOGRAPH(S) AS DRAWING(S)." 37 C.F.R. § 1.84(b).  
 formal  
 informal

### B. Other Papers Enclosed

3 Pages of declaration and power of attorney

1 Pages of abstract

— Other

### 4. Additional papers enclosed

Amendment to claims

Cancel in this applications claims 1-16 before calculating the filing fee. (At least one original independent claim must be retained for filing purposes.)  
 Add the claims shown on the attached amendment. (Claims added have been numbered consecutively following the highest numbered original claims.)  
 Preliminary Amendment  
 Information Disclosure Statement (37 C.F.R. § 1.98)  
 Form PTO-1449 (PTO/SB/08A and 08B)  
 Citations

- Declaration of Biological Deposit
- Submission of "Sequence Listing," computer readable copy and/or amendment pertaining thereto for biotechnology invention containing nucleotide and/or amino acid sequence.
- Authorization of Attorney(s) to Accept and Follow Instructions from Representative
- Special Comments
- Other

## 5. Declaration or oath (including power of attorney)

NOTE: A newly executed declaration is not required in a continuation or divisional application provided that the prior nonprovisional application contained a declaration as required, the application being filed is by all or fewer than all the inventors named in the prior application, there is no new matter in the application being filed, and a copy of the executed declaration filed in the prior application (showing the signature or an indication thereon that it was signed) is submitted. The copy must be accompanied by a statement requesting deletion of the names of person(s) who are not inventors of the application being filed. If the declaration in the prior application was filed under § 1.47, then a copy of that declaration must be filed accompanied by a copy of the decision granting § 1.47 status or, if a nonsigning person under § 1.47 has subsequently joined in a prior application, then a copy of the subsequently executed declaration must be filed. See 37 C.F.R. §§ 1.63(d)(1)–(3).

NOTE: A declaration filed to complete an application must be executed, identify the specification to which it is directed, identify each inventor by full name including family name and at least one given name, without abbreviation together with any other given name or initial, and the residence, post office address and country or citizenship of each inventor, and state whether the inventor is a sole or joint inventor. 37 C.F.R. § 1.63(a)(1)–(4).

NOTE: "The inventorship of a nonprovisional application is that inventorship set forth in the oath or declaration as prescribed by § 1.62, except as provided for in § 1.53(d)(4) and § 1.63(d). If an oath or declaration as prescribed by § 1.63 is not filed during the pendency of a nonprovisional application, the inventorship is that inventorship set forth in the application papers filed pursuant to § 1.53(b), unless a petition under this paragraph accompanied by the fee set forth in § 1.17(l) is filed supplying or changing the name or names of the inventor or inventors." 37 C.F.R. § 1.41(a)(1).

Enclosed

Executed by

(check all applicable boxes)

- inventor(s).
- legal representative of inventor(s).  
37 C.F.R. §§ 1.42 or 1.43.
- joint inventor or person showing a proprietary interest on behalf of inventor who refused to sign or cannot be reached.
  - This is the petition required by 37 C.F.R. § 1.47 and the statement required by 37 C.F.R. § 1.47 is also attached. See item 13 below for fee.
- Not Enclosed.

NOTE: Where the filing is a completion in the U.S. of an International Application or where the completion of the U.S. application contains subject matter in addition to the International Application, the application may be treated as a continuation or continuation-in-part, as the case may be, utilizing ADDED PAGE FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION CLAIMED.

- Application is made by a person authorized under 37 C.F.R. § 1.41(c) on behalf of all the above named inventor(s).

(The declaration or oath, along with the surcharge required by 37 C.F.R. § 1.16(e) can be filed subsequently).

Showing that the filing is authorized.  
(not required unless called into question. 37 C.F.R. § 1.41(d))

#### 6. Inventorship Statement

**WARNING:** If the named inventors are each not the inventors of all the claims an explanation, including the ownership of the various claims at the time the last claimed invention was made, should be submitted.

The inventorship for all the claims in this application are:

The same.  
or  
 Not the same. An explanation, including the ownership of the various claims at the time the last claimed invention was made,  
 is submitted.  
 will be submitted.

#### 7. Language

**NOTE:** An application including a signed oath or declaration may be filed in a language other than English. An English translation of the non-English language application and the processing fee of \$130.00 required by 37 C.F.R. § 1.17(k) is required to be filed with the application, or within such time as may be set by the Office. 37 C.F.R. § 1.52(d).

English  
 Non-English  
 The attached translation includes a statement that the translation is accurate. 37 C.F.R. § 1.52(d).

#### 8. Assignment

An assignment of the invention to Kerr-McGee Chemical LLC

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is attached. A separate  "COVER SHEET FOR ASSIGNMENT (DOCUMENT) ACCOMPANYING NEW PATENT APPLICATION" or  FORM PTO 1595 is also attached.  
 will follow.

**NOTE:** "If an assignment is submitted with a new application, send two separate letters-one for the application and one for the assignment." Notice of May 4, 1990 (1114 O.G. 77-78).

**WARNING:** A newly executed "CERTIFICATE UNDER 37 C.F.R. § 3.73(b)" must be filed when a continuation-in-part application is filed by an assignee. Notice of April 30, 1993, 1150 O.G. 62-64.

## 9. Certified Copy

Certified copy(ies) of application(s)

Country	Appn. No.	Filed
Country	Appn. No.	Filed
Country	Appn. No.	Filed

from which priority is claimed

- is (are) attached.
- will follow.

NOTE: The foreign application forming the basis for the claim for priority must be referred to in the oath or declaration. 37 C.F.R. § 1.55(a) and 1.63.

NOTE: This item is for any foreign priority for which the application being filed directly relates. If any parent U.S. application or International Application from which this application claims benefit under 35 U.S.C. § 120 is itself entitled to priority from a prior foreign application, then complete item 18 on the ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

## 10. Fee Calculation (37 C.F.R. § 1.16)

### A. Regular application

CLAIMS AS FILED			
Number filed	Number Extra	Rate	Basic Fee
			37 C.F.R. § 1.16(a) <del>\$700.00</del> 690.00
Total			
Claims (37 C.F.R. § 1.16(c))	8 - 20 =	× \$ 18.00 =	0.00
Independent Claims (37 C.F.R. § 1.16(b))	8 - 3 = 5	× \$ 78.00 =	390.00
Multiple dependent claim(s), if any (37 C.F.R. § 1.16(d))		+	\$260.00

- Amendment cancelling extra claims is enclosed.
- Amendment deleting multiple-dependencies is enclosed.
- Fee for extra claims is not being paid at this time.

NOTE: If the fees for extra claims are not paid on filing they must be paid or the claims cancelled by amendment, prior to the expiration of the time period set for response by the Patent and Trademark Office in any notice of fee deficiency. 37 C.F.R. § 1.16(d).

Filing Fee Calculation \$ 1,080.00

### B. Design application (\$310.00—37 C.F.R. § 1.16(f))

Filing Fee Calculation \$

C.  Plant application  
(\$480.00—37 C.F.R. § 1.16(g))

Filing fee calculation \$ \_\_\_\_\_

**11. Small Entity Statement(s)**

Statement(s) that this is a filing by a small entity under 37 C.F.R. § 1.9 and 1.27 is (are) attached.

**WARNING:** "Status as a small entity must be specifically established in each application or patent in which the status is available and desired. Status as a small entity in one application or patent does not affect any other application or patent, including applications or patents which are directly or indirectly dependent upon the application or patent in which the status has been established. The refiling of an application under § 1.53 as a continuation, division, or continuation-in-part (including a continued prosecution application under § 1.53(d)), or the filing of a reissue application requires a new determination as to continued entitlement to small entity status for the continuing or reissue application. A nonprovisional application claiming benefit under 35 U.S.C. § 119(e), 120, 121, or 365(c) of a prior application, or a reissue application may rely on a statement filed in the prior application or in the patent if the nonprovisional application or the reissue application includes a reference to the statement in the prior application or in the patent or includes a copy of the statement in the prior application or in the patent and status as a small entity is still proper and desired. The payment of the small entity basic statutory filing fee will be treated as such a reference for purposes of this section." 37 C.F.R. § 1.28(a)(2).

**WARNING:** "Small entity status must not be established when the person or persons signing the . . . statement can unequivocally make the required self-certification." M.P.E.P., § 509.03, 6th ed., rev. 2, July 1996 (emphasis added).

(complete the following, if applicable)

Status as a small entity was claimed in prior application

\_\_\_\_\_ / \_\_\_\_\_, filed on \_\_\_\_\_, from which benefit is being claimed for this application under:

35 U.S.C. §  119(e),  
 120,  
 121,  
 365(c),

and which status as a small entity is still proper and desired.

A copy of the statement in the prior application is included.

Filing Fee Calculation (50% of A, B or C above)

\$ \_\_\_\_\_

**NOTE:** Any excess of the full fee paid will be refunded if small entity status is established and a refund request are filed within 2 months of the date of timely payment of a full fee. The two-month period is not extendable under § 1.136. 37 C.F.R. § 1.28(a).

**12. Request for International-Type Search (37 C.F.R. § 1.104(d))**

(complete, if applicable)

Please prepare an international-type search report for this application at the time when national examination on the merits takes place.

**13. Fee Payment Being Made at This Time**

Not Enclosed

No filing fee is to be paid at this time.

*(This and the surcharge required by 37 C.F.R. § 1.16(e) can be paid subsequently.)*

Enclosed

Filing fee

\$ 1,080.00

Recording assignment

*(\$40.00; 37 C.F.R. § 1.21(h))*

*(See attached "COVER SHEET FOR  
ASSIGNMENT ACCOMPANYING NEW  
APPLICATION".)*

\$ \_\_\_\_\_

Petition fee for filing by other than all the inventors or person on behalf of the inventor where inventor refused to sign or cannot be reached

*(\$130.00; 37 C.F.R. §§ 1.47 and 1.17(l))*

\$ \_\_\_\_\_

For processing an application with a specification in a non-English language

*(\$130.00; 37 C.F.R. §§ 1.52(d) and 1.17(k))*

\$ \_\_\_\_\_

Processing and retention fee

*(\$130.00; 37 C.F.R. §§ 1.53(d) and 1.21(l))*

\$ \_\_\_\_\_

Fee for international-type search report

*(\$40.00; 37 C.F.R. § 1.21(e))*

\$ \_\_\_\_\_

**NOTE:** 37 C.F.R. § 1.21(l) establishes a fee for processing and retaining any application that is abandoned for failing to complete the application pursuant to 37 C.F.R. § 1.53(f) and this, as well as the changes to 37 C.F.R. §§ 1.53 and 1.78(a)(1), indicate that in order to obtain the benefit of a prior U.S. application, either the basic filing fee must be paid, or the processing and retention fee of § 1.21(l) must be paid, within 1 year from notification under § 53(f).

Total fees enclosed \$ 1,080.00

**14. Method of Payment of Fees**

Check in the amount of \$ 1,080.00

Charge Account No. \_\_\_\_\_ in the amount of \$ \_\_\_\_\_

A duplicate of this transmittal is attached.

**NOTE:** Fees should be itemized in such a manner that it is clear for which purpose the fees are paid. 37 C.F.R. § 1.22(b).

## 15. Authorization to Charge Additional Fees

**WARNING:** If no fees are to be paid on filing, the following items should not be completed.

**WARNING:** Accurately count claims, especially multiple dependent claims, to avoid unexpected high charges, if extra claim charges are authorized.

The Commissioner is hereby authorized to charge the following additional fees by this paper and during the entire pendency of this application to Account No. 50-0449:

37 C.F.R. § 1.16(a), (f) or (g) (filing fees)

37 C.F.R. § 1.16(b), (c) and (d) (presentation of extra claims)

**NOTE:** Because additional fees for excess or multiple dependent claims not paid on filing or on later presentation must only be paid or these claims cancelled by amendment prior to the expiration of the time period set for response by the PTO in any notice of fee deficiency (37 C.F.R. § 1.16(d)), it might be best not to authorize the PTO to charge additional claim fees, except possibly when dealing with amendments after final action.

37 C.F.R. § 1.16(e) (surcharge for filing the basic filing fee and/or declaration on a date later than the filing date of the application)

37 C.F.R. § 1.17(a)(1)–(5) (extension fees pursuant to § 1.136(a)).

37 C.F.R. § 1.17 (application processing fees)

**NOTE:** ". . . A written request may be submitted in an application that is an authorization to treat any concurrent or future reply, requiring a petition for an extension of time under this paragraph for its timely submission, as incorporating a petition for extension of time for the appropriate length of time. An authorization to charge all required fees, fees under § 1.17, or all required extension of time fees will be treated as a constructive petition for an extension of time in any concurrent or future reply requiring a petition for an extension of time under this paragraph for its timely submission. Submission of the fee set forth in § 1.17(a) will also be treated as a constructive petition for an extension of time in any concurrent reply requiring a petition for an extension of time under this paragraph for its timely submission." 37 C.F.R. § 1.136(a)(3).

37 C.F.R. § 1.18 (issue fee at or before mailing of Notice of Allowance, pursuant to 37 C.F.R. § 1.311(b))

**NOTE:** Where an authorization to charge the issue fee to a deposit account has been filed before the mailing of a Notice of Allowance, the issue fee will be automatically charged to the deposit account at the time of mailing the notice of allowance. 37 C.F.R. § 1.311(b).

**NOTE:** 37 C.F.R. § 1.28(b) requires "Notification of any change in status resulting in loss of entitlement to small entity status must be filed in the application . . . prior to paying, or at the time of paying, . . . the issue fee. . . ." From the wording of 37 C.F.R. § 1.28(b), (a) notification of change of status must be made even if the fee is paid as "other than a small entity" and (b) no notification is required if the change is to another small entity.

**16. Instructions as to Overpayment**

NOTE: ". . . Amounts of twenty-five dollars or less will not be returned unless specifically requested within a reasonable time, nor will the payer be notified of such amounts; amounts over twenty-five dollars may be returned by check or, if requested, by credit to a deposit account." 37 C.F.R. § 1.26(a).

Credit Account No. 50-0449  
 Refund

C. Clark Dougherty, Jr.  
SIGNATURE OF PRACTITIONER

Reg. No. 24,208

C. Clark Dougherty, Jr.

(type or print name of attorney)

MCAFEE & TAFT

Two Leadership Square

P.O. Address

211 N. Robinson, Tenth Floor  
Oklahoma City, Oklahoma 73102

Customer No.

**Incorporation by reference of added pages**

*(check the following item if the application in this transmittal claims the benefit of, prior U.S. application(s) (including an international application entering the U.S. stage as a continuation, divisional or C-I-P application) and complete and attach the ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED)*

Plus Added Pages for New Application Transmittal Where Benefit of Prior U.S. Application(s) Claimed

Number of pages added 5

Plus Added Pages for Papers Referred to in Item 4 Above

Number of pages added \_\_\_\_\_

Plus added pages deleting names of inventor(s) named in prior application(s) who is/are no longer inventor(s) of the subject matter claimed in this application.

Number of pages added \_\_\_\_\_

Plus "Assignment Cover Letter Accompanying New Application"

Number of pages added \_\_\_\_\_

**Statement Where No Further Pages Added**

*(if no further pages form a part of this Transmittal, then end this Transmittal with this page and check the following item)*

This transmittal ends with this page.

**ADDED PAGES FOR APPLICATION TRANSMITTAL WHERE BENEFIT OF  
PRIOR U.S. APPLICATION(S) CLAIMED**

NOTE: See 37 CFR 1.78.

**17. Relate Back**

**WARNING:** *If an application claims the benefit of the filing date of an earlier filed application under 35 U.S.C. 120, 121 or 365(c), the 20-year term of that application will be based upon the filing date of the earliest U.S. application that the application makes reference to under 35 U.S.C. 120, 121 or 365(c). (35 U.S.C. 154(a)(2) does not take into account, for the determination of the patent term, any application on which priority is claimed under 35 U.S.C. 119, 365(a) or 365(b).) For a c-i-p application, applicant should review whether any claim in the patent that will issue is supported by an earlier application and, if not, the applicant should consider canceling the reference to the earlier filed application. The term of a patent is not based on a claim-by-claim approach. See Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,205.*

*(complete the following, if applicable)*

Amend the specification by inserting, before the first line, the following sentence:

**A. 35 U.S.C. 119(e)**

**NOTE:** *"Any nonprovisional application claiming the benefit of one or more prior filed copending provisional applications must contain or be amended to contain in the first sentence of the specification following the title a reference to each such prior provisional application, identifying it as a provisional application, and including the provisional application number (consisting of series code and serial number)." 37 C.F.R. § 1.78(a)(4).*

"This application claims the benefit of U.S. Provisional Application(s) No(s).:

**APPLICATION NO(S):**

**FILING DATE**

\_\_\_\_ / \_\_\_\_\_

\_\_\_\_ " \_\_\_\_\_

\_\_\_\_ / \_\_\_\_\_

\_\_\_\_ " \_\_\_\_\_

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\_\_\_\_ " \_\_\_\_\_

**B. 35 U.S.C. 120, 121 and 365(c)**

**NOTE:** "Except for a continued prosecution application filed under § 1.53(d), any nonprovisional application claiming the benefit of one or more prior filed copending nonprovisional applications or international applications designating the United States of America must contain or be amended to contain in the first sentence of the specification following the title a reference to each such prior application, identifying it by application number (consisting of the series code and serial number) or international application number and international filing date and indicating the relationship of the applications. . . . Cross-references to other related applications may be made when appropriate." (See § 1.14(a)). 37 C.F.R. § 1.78(a)(2).

"This application is a

continuation

continuation-in-part

divisional

of copending application(s)

application number 09 / 217,168 filed on December 21, 1998,

International Application \_\_\_\_\_ filed on \_\_\_\_\_

and which designated the U.S."

**NOTE:** The proper reference to a prior filed PCT application that entered the U.S. national phase is the U.S. serial number and the filing date of the PCT application that designated the U.S.

**NOTE:** (1) Where the application being transmitted adds subject matter to the International Application, then the filing can be as a continuation-in-part or (2) if it is desired to do so for other reasons then the filing can be as a continuation.

**NOTE:** The deadline for entering the national phase in the U.S. for an international application was clarified in the Notice of April 28, 1987 (1079 O.G. 32 to 46) as follows:

"The Patent and Trademark Office considers the International application to be pending until the 22nd month from the priority date if the United States has been designated and no Demand for International Preliminary Examination has been filed prior to the expiration of the 19th month from the priority date and until the 32nd month from the priority date if a Demand for International Preliminary Examination which elected the United States of America has been filed prior to the expiration of the 19th month from the priority date, provided that a copy of the international application has been communicated to the Patent and Trademark Office within the 20 or 30 month period respectively. If a copy of the international application has not been communicated to the Patent and Trademark Office within the 20 or 30 month period respectively, the international application becomes abandoned as to the United States 20 or 30 months from the priority date respectively. These periods have been placed in the rules as paragraph (h) of § 1.494 and paragraph (i) of § 1.495. A continuing application under 35 U.S.C. 365(c) and 120 may be filed anytime during the pendency of the international application."

"The nonprovisional application designated above, namely application

\_\_\_\_\_ / \_\_\_\_\_, filed \_\_\_\_\_, claims the benefit of U.S. Provisional Application(s) No(s):

**APPLICATION NO(S):**

**FILING DATE**

\_\_\_\_\_ / \_\_\_\_\_

\_\_\_\_\_ "

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\_\_\_\_\_ / \_\_\_\_\_

\_\_\_\_\_ "

Where more than one reference is made above, please combine all references into one sentence.

## 18. Relate Back—35 U.S.C. 119 Priority Claim for Prior Application

The prior U.S. application(s), including any prior International Application designating the U.S., identified above in item 17B, in turn itself claim(s) foreign priority(ies) as follows:

Country	Appln. no.	Filed on
---------	------------	----------

The certified copy(ies) has (have)

- been filed on \_\_\_\_\_, in prior application 0 / \_\_\_\_\_, which was filed on \_\_\_\_\_.
- is (are) attached.

**WARNING:** *The certified copy of the priority application that may have been communicated to the PTO by the International Bureau may not be relied on without any need to file a certified copy of the priority application in the continuing application. This is so because the certified copy of the priority application communicated by the International Bureau is placed in a folder and is not assigned a U.S. serial number unless the national stage is entered. Such folders are disposed of if the national stage is not entered. Therefore, such certified copies may not be available if needed later in the prosecution of a continuing application. An alternative would be to physically remove the priority documents from the folders and transfer them to the continuing application. The resources required to request transfer, retrieve the folders, make suitable record notations, transfer the certified copies, enter and make a record of such copies in the Continuing Application are substantial. Accordingly, the priority documents in folders of international applications that have not entered the national stage may not be relied on. Notice of April 28, 1987 (1079 O.G. 32 to 46).*

## 19. Maintenance of Copendency of Prior Application

**NOTE:** *The PTO finds it useful if a copy of the petition filed in the prior application extending the term for response is filed with the papers constituting the filing of the continuation application. Notice of November 5, 1985 (1060 O.G. 27).*

### A. Extension of time in prior application

*(This item must be completed and the papers filed in the prior application, if the period set in the prior application has run.)*

- A petition, fee and response extends the term in the pending prior application until \_\_\_\_\_.
- A copy of the petition filed in prior application is attached.

### B. Conditional Petition for Extension of Time in Prior Application

*(complete this item, if previous item not applicable)*

- A conditional petition for extension of time is being filed in the pending prior application.
- A copy of the conditional petition filed in the prior application is attached.

**20. Further Inventorship Statement Where Benefit of Prior Application(s) Claimed**

*(complete applicable item (a), (b) and/or (c) below)*

(a)  This application discloses and claims only subject matter disclosed in the prior application whose particulars are set out above and the inventor(s) in this application are  
 the same.  
 less than those named in the prior application. It is requested that the following inventor(s) identified for the prior application be deleted:

---

*(type name(s) of inventor(s) to be deleted)*

(b)  This application discloses and claims additional disclosure by amendment and a new declaration or oath is being filed. With respect to the prior application, the inventor(s) in this application are  
 the same.  
 the following additional inventor(s) have been added:

---

*(type name(s) of inventor(s) to be added)*

(c) The inventorship for all the claims in this application are  
 the same.  
 not the same. An explanation, including the ownership of the various claims at the time the last claimed invention was made  
 is submitted.  
 will be submitted.

**21. Abandonment of Prior Application (if applicable)**

Please abandon the prior application at a time while the prior application is pending, or when the petition for extension of time or to revive in that application is granted, and when this application is granted a filing date, so as to make this application copending with said prior application.

NOTE: According to the Notice of May 13, 1983 (103, TMOG 6-7), the filing of a continuation or continuation-in-part application is a proper response with respect to a petition for extension of time or a petition to revive and should include the express abandonment of the prior application conditioned upon the granting of the petition and the granting of a filing date to the continuing application.

**22. Petition for Suspension of Prosecution for the Time Necessary to File an Amendment**

**WARNING:** "The claims of a new application may be finally rejected in the first Office action in those situations where (1) the new application is a continuing application of, or a substitute for, an earlier application, and (2) all the claims of the new application (a) are drawn to the same invention claimed in the earlier application, and (b) would have been properly finally rejected on the grounds of art of record in the next Office action if they had been entered in the earlier application." MPEP, § 706.07(b), 6th ed., rev.2.

NOTE: Where it is possible that the claims on file will give rise to a first action final for this continuation application and for some reason an amendment cannot be filed promptly (e.g., experimental data is being gathered) it may be desirable to file a petition for suspension of prosecution for the time necessary.

(check the next item, if applicable)

There is provided herewith a Petition To Suspend Prosecution for the Time Necessary to File An Amendment (New Application Filed Concurrently)

**23. Small Entity (37 CFR § 1.28(a))**

Applicant has established small entity status by the filing of a statement in parent application / \_\_\_\_\_ on \_\_\_\_\_.  
 A copy of the statement previously filed is included.

**WARNING:** See 37 CFR § 1.28(a).

**24. NOTIFICATION IN PARENT APPLICATION OF THIS FILING**

A notification of the filing of this  
(check one of the following)

continuation  
 continuation-in-part  
 divisional

is being filed in the parent application, from which this application claims priority under 35 U.S.C. § 120.

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re application of: Terrell N. Andersen et al.  
Serial No.: 09 /217,168 Group No.: 1741  
Filed: December 21, 1998 Examiner: William Leader  
For: HIGH DISCHARGE CAPACITY ELECTROLYTIC MANGANESE DIOXIDE AND METHODS OF  
PRODUCING THE SAME  
Assistant Commissioner for Patents  
Washington, D.C. 20231

**NOTIFICATION OF FILING OF CONTINUING,  
DIVISIONAL OR CONTINUED PROSECUTION APPLICATION**

Notification is hereby being made of the filing of a:

continuation  
 continuation-in-part  
 divisional  
 continued prosecution

application for this case

concurrently herewith.  
 on \_\_\_\_\_

Date

---

**CERTIFICATION UNDER 37 CFR 1.8(a) and 1.10**

*(When using Express Mail, the Express Mail label number is mandatory;  
Express Mail certification is optional.)*

I hereby certify that, on the date shown below, this correspondence is being:

**MAILING**

deposited with the United States Postal Service in an envelope addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231  
37 CFR 1.8(a)

with sufficient postage as first class mail.  as "Express Mail Post Office to Addressee"  
Mailing Label No. EL 495 102 459 US (mandatory)

**TRANSMISSION**

transmitted by facsimile to the Patent and Trademark Office.



Signature

Dana M. Coots

(type or print name of person certifying)

**\*WARNING:** Each paper or fee filed by Express Mail **must** have the number of the "Express Mail" mailing label placed thereon prior to mailing. 37 C.F.R. 1.10(b).

"Since the filing of correspondence under § 1.10 without the Express Mail mailing label thereon is an oversight that can be avoided by the exercise of reasonable care, requests for waiver of this requirement will **not** be granted on petition." Notice of Oct. 24, 1996, 60 Fed. Reg. 56,439, at 56,442.

Reg. No. 24,208

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SIGNATURE OF PRACTITIONER

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Terrell N. Andersen et al. )  
Serial No.: Unknown ) Art Unit: 1741  
Filed: Concurrently Herewith )  
For: HIGH DISCHARGE CAPACITY )  
ELECTROLYTIC MANGANESE ) Examiner: William Leader  
DIOXIDE AND METHODS OF )  
PRODUCING THE SAME )

**PRELIMINARY AMENDMENT**

Box Patent Application  
Commissioner for Patents  
Washington, D.C. 20231

Sir:

**In the Claims:**

Please add the following new claims:

--21. An improved cathode material comprising EMD having a % MnO<sub>2</sub> of about 91.9 or higher.

22. An improved cathode material comprising EMD having a % Mn of about 60.1 or lower.

23. An improved cathode material comprising EMD having a % structural H<sub>2</sub>O of about 3.28 or lower.

---

**CERTIFICATE OF MAILING (37 C.F.R. §1.10)**

I hereby certify that this correspondence is being deposited with the United States Postal Service in an envelope as "Express Mail Post Office to Addressee," mailing Label Number EL 495 102 459 US, addressed to: Box Patent Application, Commissioner for Patents, Washington, D.C. 20231, on the date indicated below.

*Dana M. Coots*

Signature

July 6, 2000

*July 6, 2000*

*Dana M. Coots*  
Name of Person Certifying

24. An improved cathode material comprising EMD having a BET surface area of about 23.5 sq. meters per gram or lower.

25. An improved cathode material comprising EMD having a total pore volume of 27 cubic centimeters per kilogram or lower.--

**Remarks**

The antecedent basis for the new claims set forth above is found in the specification and particularly in Example 2 beginning on page 28 and Table III set forth at page 31.

The entry of this Preliminary Amendment and the allowance of claims 17-25 are respectfully requested.

Respectfully submitted,

*C. Clark Dougherty Jr.*  
C. Clark Dougherty, Jr.  
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**ATTORNEY FOR APPLICANTS**

PATENT  
Case No. 1060HIGH DISCHARGE CAPACITY ELECTROLYTIC  
MANGANESE DIOXIDE AND METHODS OF PRODUCING THE SAME

## Background of the Invention

1. Field of the Invention.

5        The present invention relates to electrolytic manganese dioxide for use as the cathode in batteries and methods of producing the electrolytic manganese dioxide. More particularly, the present invention provides electrolytic manganese dioxide which when utilized in batteries imparts higher discharge capacity at high discharge rates thereto.

2. Description of the Prior Art.

15        Electrolytic manganese dioxide, referred to in the industry as EMD, is widely used as the cathode material in batteries. EMD was first utilized in zinc-carbon cells (Leclanche cells), and later in alkaline cells.

20        EMD is used in alkaline batteries to achieve high voltages, low polarization and high discharge capacities. The discharge capacity of alkaline batteries is dependent upon the quality of the EMD utilized. The mixture forming the cathode in alkaline batteries is about 82% EMD and is generally formed into an annular cathode by impact extrusion in the container or by the compression molding of

pellets which are recompacted against the container. In both of these processes, the properties of the EMD must be very consistent to allow the battery manufacturer to consistently produce high quality batteries. Alkaline batteries have a higher capacity per unit volume than other zinc-manganese dioxide batteries, and are particularly capable of high discharge capacity, i.e., long life, at high discharge rates.

To achieve the EMD purity required in its production utilizing the well known electrolysis method, a highly purified manganese sulfate solution must be provided to the electrolytic cell. In addition, the electrolytic cell must be operated within a narrow range of process conditions.

By the end of the 1980's, EMD was developed having what was thought to be a satisfactory discharge capacity at the then maximum discharge rates demanded by portable devices, i.e., about 0.5 watt. However, during the past several years, the development of lap-top computers, video cameras, cellular phones and the like have brought about a demand for high discharge capacity at higher discharge rates, i.e., from 1 to 2 watts. While some improvements in battery performance at high discharge rates have been made, EMD has not changed significantly in discharge capacity or in the process conditions utilized in its production for many years. Thus, there is a continuing need for better, higher quality EMD whereby alkaline and other batteries

utilizing the EMD have higher discharge capacities at the higher discharge rates presently required.

#### Summary of the Invention

The present invention provides improved high quality EMD for use as cathode material in batteries of high discharge capacity at high discharge rates and methods of producing such EMD by electro-deposition in an electrolytic cell. The electrolytic cell includes cathodic and anodic electrodes disposed therein through which an electric current is passed. In accordance with the methods of the present invention, a heated aqueous electrolyte solution comprising sulfuric acid and manganese sulfate is maintained in the electrolytic cell. The solution is of high purity and includes manganese sulfate therein in an amount whereby manganese is present in the range of from about 5 to about 50 grams of manganese per liter of solution. An electric current is applied to the cathodic and anodic electrodes and the electrolyte solution whereby the anodic electrode current density is in the range of from about 2.5 to about 6 amperes per square foot, and the high discharge capacity EMD produced is deposited on the anode.

The temperature of the electrolyte solution in the electrolytic cell is carefully maintained in the range of from about 95°C to about 98°C. Also, the sulfuric acid

concentration in the electrolyte solution is maintained in an amount in the range of from about 20 to about 50 grams of sulfuric acid per liter of solution.

5 The cathode utilized in the electrolytic cell is preferably comprised of copper, graphite or steel, as determined by cost. The anode is preferably comprised of titanium to provide minimum weight and volume, maximum strength, minimum weight loss, and adequate corrosion resistance.

10 It is, therefore, a general object of the present invention to provide improved electrolytic manganese dioxide having higher discharge capacity at high discharge rates and methods of producing the same.

15 Other and further objects, features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of preferred embodiments which follows.

#### **Brief Description of the Drawings**

20 FIGURE 1 is a plot of relative discharge energy in AA cells vs. the EMD deposition current density at 95°C, 30 g/l  $H_2SO_4$  and 30 g/l  $Mn^{2+}$  as obtained from multiple regression of the experimental results (Table II) in the current density range of 2.5-6.0  $A/ft^2$ .

25 FIGURE 2 is a topographical representation of the relative energy in AA cells vs. the  $H_2SO_4$  and  $Mn^{2+}$

concentrations as obtained from multiple regression of the experimental results (Table II) within the current density range of 2.5-6.0 A/ft<sup>2</sup>.

5 FIGURE 3 is a scatter plot of the experimental relative discharge energies in AA cells vs. the BET surface areas of all the EMD samples in Table II. The open circle represents the reference Sample No. 41 in this and subsequent figures.

10 FIGURE 4 is a scatter plot of the experimental relative discharge energies in AA cells vs. the compressed densities of the EMD samples.

15 FIGURE 5 is a scatter plot of the experimental relative discharge energies in AA cells vs. the initial open circuit voltages of the EMD samples.

FIGURE 6 is a scatter plot of the experimental relative discharge energies in AA cells vs. the intrinsic discharge capacities of the EMD samples.

20 FIGURE 7 is a scatter plot of the experimental relative discharge energies in AA cells vs. the Q-ratio of the EMD samples.

FIGURE 8 is a scatter plot of the experimental relative discharge energies in AA cells vs. the structural water content of the EMD samples.

25 FIGURE 9 is a scatter plot of the experimental relative discharge energies in AA cells vs. the MnO<sub>2</sub> content of the EMD samples.

FIGURE 10 is an XRD scan of Sample No. 16, deposited under the conditions of the invention, i.e., 3.4 A/ft<sup>2</sup>, 96°C, 29 g/l H<sub>2</sub>SO<sub>4</sub> and 9 g/l Mn<sup>2+</sup>.

FIGURE 11 is an XRD scan of Sample No. 4, deposited at 5 3.4 A/ft<sup>2</sup>, 96°C, 12 g/l H<sub>2</sub>SO<sub>4</sub> and 9 g/l Mn<sup>2+</sup>.

#### Description of Preferred Embodiments

Electrolytic manganese dioxide (EMD) is produced by subjecting an aqueous electrolyte solution comprised of sulfuric acid and manganese sulfate to electrolysis in an electrolytic cell having cathodic and anodic electrodes disposed therein. The electrolysis process causes oxidation of the manganese sulfate at the anodic electrode and the deposition of a coating of the desired manganese dioxide product on the anode. When the coating has built 10 up to a desired thickness, the anode is removed from the electrolytic cell and the coating is removed therefrom.

As mentioned above, it is imperative that the manganese sulfate supplied to the electrolytic cell is of high purity. Further, it is imperative that the cathode 20 and anode in the electrolytic cell resist corrosion. As a result, various methods of producing manganese sulfate solutions of improved purity have heretofore been developed. For example, United States Patents Nos. 4,483,828 issued on November 20, 1984 to Laughlin et al., 25 4,485,073 issued on November 27, 1984 to Robertson et al.

and 4,489,043 issued on December 18, 1984 to Bowerman et al. are all directed to methods of producing high purity manganese sulfate solutions and are all assigned to Kerr-McGee Chemical Corporation. U.S. Patent No. 4,606,804 issued December 18, 1984 to Schulke and Spore, and U.S. Patent No. 4,477,320 issued October 16, 1984 to Riggs, Jr. and assigned to Kerr-McGee Chemical Corporation disclose an improved anode formed of titanium and an improved cathode formed of copper, respectively. All of the above mentioned 5 patents are incorporated herein by reference and are to be taken and considered as a part hereof as if they were fully 10 set out herein.

To produce high purity EMD having high discharge capacity suitable for use in alkaline batteries, the electrolytic cell must be operated within a rather narrow 15 range of conditions. Typical electrolytic cell conditions used in the industry for producing alkaline-battery grade EMD are given by E. Preisler in *J. Applied Electrochemistry*, Vol. 19 (1989) pp. 559-565. These 20 conditions are a temperature of 90-95°C, a current density of 6.5-9.3 A/ft<sup>2</sup>, a sulfuric acid concentration of 9.8-39 g/l and a manganese ion concentration of 27-55 g/l. Titanium anodes were used. Other publications present 25 conditions that are equivalent or nearly equivalent to these.

Very recently Takehara et al. (United States Patent No. 5,746,902 issued on May 5, 1998 and assigned to Japan Metals and Chemicals Company Ltd.) set forth conditions for manufacturing EMD for alkaline manganese batteries to make them excellent in both initial performance and storability. These conditions consist of a current density of 0.4 to 0.9 A/dm<sup>2</sup> (3.7 to 8.4 A/ft<sup>2</sup>), an electrolyte solution temperature of from 94°C to 103°C, an electrolyte solution sulfuric acid concentration of 0.30 to 0.45 mol/liter (29.4 to 44.1 g/l) and a manganese sulfate concentration of 0.5 to 1.0 mol/liter (27.5 to 55 g/l of manganese ions). Their temperatures and current densities were correlated inversely; i.e., they taught the use of the higher temperature with the lower current density and vice versa. These sulfuric acid and manganese ion concentrations are typical of prior art, but the lower end of the current density range is decreased somewhat and the upper temperature is increased somewhat.

These investigators also gave a set of conditions for manufacturing EMD in a so-called suspension or slurry cell, in which tiny particulates of manganese oxide are suspended in the electrolyte solution. However, this latter modification of EMD deposition does not pertain to the present invention.

The present invention is based on the discovery that improved EMD for use as cathode material in batteries

having an unexpected high capacity at high discharge rates, i.e., rates of from 1 to 3 watts in AA-cells, can be produced when a low anodic current density is utilized in combination with a low concentration of manganese sulfate in the electrolyte solution.

5

More specifically, the methods of the present invention for producing very high discharge capacity EMD by electrolysis in an electrolytic cell are basically comprised of the steps of maintaining a heated aqueous electrolyte solution comprising sulfuric acid and manganese sulfate in the electrolytic cell, the solution having manganese sulfate therein in an amount whereby manganese is present in the range of from about 5 to about 50 grams of manganese per liter of solution, and applying electric current to the electrodes whereby the anodic electrode current density is in the range of from about 2.5 to about 6 amperes per square foot and the high discharge capacity EMD produced is deposited on the anodic electrode.

10

15

The aqueous electrolyte solution is maintained in the electrolytic cell at a temperature in the range of from about 95°C to about 98°C. Also, the concentration of sulfuric acid in the aqueous electrolyte solution is maintained in the range of from about 20 to about 60 grams of sulfuric acid per liter of solution.

20

25

In order to insure that the above described conditions are consistently maintained, the anodic electrode utilized

in the electrolysis process is preferably comprised of titanium as described in the above mentioned U.S. Patent No. 4,606,804, and the cathodic electrode is preferably comprised of copper as described in the above mentioned U.S. Patent No. 4,477,320.

More preferred electrolysis conditions for carrying out the methods of this invention include maintaining the manganese sulfate in the aqueous electrolyte solution in an amount whereby manganese is present in the range of from about 5 to about 20 grams of manganese per liter of solution, applying electric current to the electrodes whereby the anodic electrode current density is in the range of from about 2.5 to about 3.5 amperes per square foot, maintaining the electrolytic solution at a temperature in the range of from about 95°C to about 98°C and maintaining the sulfuric acid concentration in the electrolyte solution in an amount in the range of from about 25 to about 40 grams of sulfuric acid per liter of solution. In addition, the concentration of the sulfuric acid in the electrolytic solution is maintained at a level greater than or equal to two times the concentration of manganese therein.

Some of the unexpected average properties of the improved EMD of this invention having high discharge capacity at high discharge rates produced by the methods of this invention are set forth in Table I below. For

comparison purposes, the same properties of the best high discharge capacity EMD produced using prior art electrolysis conditions are also set forth in Table I. Detailed descriptions of the test methods and properties as well as individual sample results are given below. Standard deviations ( $\sigma$ ) associated with each property are listed so that the statistical significance of differences in the two products can be discerned.

TABLE I

	EMD Properties	EMD of the Present Invention (12 samples)	Prior Art EMD (18 samples)
10	AA-Cell Discharge Capacity at 1 Watt Discharge Rate (mAh/g)	68.2 $\sigma=4.4$	63.4 $\sigma=7.0$
15	AA-Cell Discharge Energy at 1 Watt Discharge Rate (mWh)	755 $\sigma=19$	637 $\sigma=6.9$
20	Intrinsic Discharge Capacity (mAh/g)	254.6 $\sigma=2.0$	248.8 $\sigma=3.6$
25	Initial Open Circuit Voltage (V vs. Zn)	1.639 $\sigma=0.006$	1.623 $\sigma=0.012$
	Compressed Density (g/cm <sup>3</sup> )	3.162 $\sigma=0.035$	3.080 $\sigma=0.021$

From Table I it can be seen that the properties of the high discharge capacity EMD produced in accordance with the methods of this invention are considerably better than the

properties of high discharge capacity EMD produced using prior art methods. For example, the higher 1-watt discharge capacity and energy translate into longer running times in high rate applications, while the higher intrinsic  
5 discharge capacity ensures a greater capacity/running time at lower-rate applications. The greater initial open circuit voltage is valued by battery makers (and is part of the reason for the greater capacities). The compressed density of the EMD is higher, which is very important from the standpoint of its use in batteries, i.e., more EMD can  
10 be placed in each cell.

A preferred method of this invention for producing EMD having a high discharge capacity at high discharge rates by electrolysis in an electrolytic cell having cathodic and anodic electrodes disposed therein is comprised of the steps of maintaining a heated aqueous electrolyte solution comprising sulfuric acid and manganese sulfate in said electrolytic cell, the solution having manganese sulfate therein in an amount whereby manganese ion is present in  
15 the range of from about 5 to about 50 grams of manganese ion per liter of solution; and applying electric current to the electrodes whereby the anodic electrode current density is in the range of from about 2.5 to about 6 amperes per square foot and the high discharge capacity electrolytic  
20 manganese dioxide produced is deposited on the anodic electrode.  
25

A more preferred method of the present invention comprises the steps of maintaining an aqueous solution comprised of sulfuric acid and manganese sulfate in the electrolytic cell at a temperature in the range of from about 95°C to about 98°C, the solution having sulfuric acid therein in an amount in the range of from about 20 to about 60 grams of sulfuric acid per liter of solution and having manganese sulfate therein in an amount whereby manganese ion is present in the range of from about 5 to about 50 grams of manganese ion per liter of solution; and applying electric current to the electrodes whereby the anodic electrode current density is in the range of from about 2.5 to about 4.5 amperes per square foot and the high discharge capacity electrolytic manganese dioxide produced is deposited on the anodic electrode.

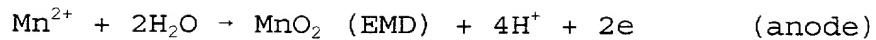
The most preferred method of the present invention for producing EMD having a high discharge capacity at high discharge rates by electrolysis in an electrolytic cell containing cathodic and anodic electrodes comprises the steps of maintaining an aqueous solution comprised of sulfuric acid and manganese sulfate in the electrolytic cell at a temperature in the range of from about 95°C to about 98°C, the electrolyte solution having sulfuric acid therein in an amount in the range of from about 25 to about 40 grams of sulfuric acid per liter of solution, having manganese sulfate therein in an amount whereby manganese

ion is present in the range of from about 5 to about 20 grams of manganese ion per liter of solution, the amount of sulfuric acid in the electrolyte solution being greater than or equal to two times the amount of manganese ion therein; and applying electric current to the electrodes whereby the anodic electrode current density is in the range of from about 2.5 to about 3.5 amperes per square foot and the high discharge capacity EMD produced is deposited on the anodic electrode.

The EMD of this invention has a discharge capacity in an AA-cell at 1 watt discharge rate of about 68.2 mAh/g-EMD and a discharge energy at a 1 watt discharge rate of about 755 mWh.

#### Experimental Procedures

Sample Preparation: EMD was deposited in bench cells that contained a titanium anode, two copper cathodes, and an aqueous electrolyte of high purity manganese sulfate ( $MnSO_4$ ) and sulfuric acid ( $H_2SO_4$ ). The cell consisted of a 4-liter battery jar, which contained the vertically suspended electrodes. The anode was a corrugated sheet of titanium 25 cm x 9.2 cm, and each of the two opposing cathodes consisted of two copper plates, 25 cm x 2 cm. Deposition for each test was conducted continuously for several weeks, the electrode reactions being



In order to maintain constant electrolyte composition in the cell throughout each test, a concentrated solution of weakly acidic  $\text{MnSO}_4$  was circulated continuously into the cell and electrolyte was removed by way of an overflow. The electrolyte concentration was monitored daily, and stayed within 1 g/l of the target  $\text{Mn}^{2+}$  and acid concentrations. Temperature in the cell was maintained by means of an immersion heater coupled with a thermoregulator. A thin layer of paraffin was maintained on top of the electrolyte to prevent evaporation. Current was supplied to the electrodes by means of a constant current power supply. Deposition cycles were generally three weeks. However, for many of the higher current density tests, the time was two weeks or less; also, for several very low current density tests, the deposition time was longer than three weeks. There is no indication that product quality varied with deposition time between 2 and 3 weeks. Thus, it was assumed that properties of the product depend only on the deposition parameters coupled with random imprecision.

At the end of the deposition time, each anode was soaked in hot water to remove the paraffin, and then the deposit was removed from the titanium anode, crushed, ground, screened, blended and neutralized with a  $\text{NaOH}$

solution to pH 7. The final product had the following particle size distribution: 9% -100/+200 mesh, 25% -200/+325 mesh and 66% -325 mesh.

More than 50 laboratory EMD samples were deposited over a wide range of deposition parameters, i.e., current density (i), temperature (T), sulfuric acid concentration ( $[H_2SO_4]$ ) and  $Mn^{2+}$ -ion concentration ( $[Mn^{2+}]$ ). After the trend of battery performance vs. deposition parameters became apparent, several pilot cells of commercial height but scaled down width and thickness were constructed, and product was deposited at favorable deposition parameters according to this invention. Care was taken to control the deposition so that the conditions did not vary over the plating cycle. Then the EMD anodes were harvested and finished as they had been in the case of laboratory cells. Additionally, several EMD samples from Kerr-McGee Chemical Corporation's production facility were selected for study, to confirm that the deposition parameters in the laboratory cells scaled commercially.

AA-Cell Tests: All of the above samples were evaluated in AA-size cylindrical cells, which were assembled in the laboratory from commercial hardware. First, the EMD was blended with Lonza KS-44 graphite and 9M KOH solution to form a cathode mix, the proportions by weight being EMD/graphite/9M KOH=85.8/7.3/6.9. These mixes were next formed into cathodes to be pressed into the steel cells.

The insides of the steel cell walls were pre-plated with nickel and pre-coated with a carbon slurry before the cathodes were pressed into the cell. This was done to improve cathode-cell electrical contact. The cathode in each case was of constant thickness and constant height (and therefore of constant volume). The contacts to the battery terminals were made by conventional means. Each cell also contained an anode composed of a zinc gel and a separator. Finally, the cells were closed in a manner analogous to that used with commercial alkaline AA cells.

The newly constructed AA cells were allowed to rest (equilibrate) for two to three days, and then were connected to a computerized Maccor battery test system and discharged at a rate of 1 watt. The discharge capacities and energies were determined at a cutoff voltage of 0.90V. Cells were made and discharged in weekly batches, with five cells per EMD sample and five EMD samples per week. Since many weeks were required to test all the EMD's, one sample was used as an internal standard and tested weekly along with the test samples for that week. The mean discharge energy (as well as the closely related discharge capacity) for the standard fluctuated somewhat from week to week, but averaged 0.675 Wh. The mean result for all cells of each test sample was divided by the mean result for the standard that was discharged in the same batch. This yielded a relative 1-watt discharge energy for each test sample.

Half-cell Tests: Some of the samples were discharged in flooded half-cells. In "half-cell tests" the EMD is discharged and its potential is measured with respect to a fixed reference electrode. Thus, all the potential change is associated with the EMD discharge, as opposed to the full-cell (i.e., AA-cell) tests, in which the voltage change is shared by both the EMD cathode and zinc anode. Flooded half-cell tests are not influenced by the balance between anode, cathode and electrolyte. Accordingly, these tests were conducted to complement the AA-cell tests. The test cathode consisted of a nickel screen, into which was pressed a blended mixture of EMD, graphite, Teflon powder (as binder), and 9M KOH in the ratio EMD/graphite/Teflon/electrolyte=8.0/1.5/0.5/1.0. The cathode, having a diameter of 1.4 cm, contained a constant weight of EMD in each case, i.e., 0.727 g, and was approximately 1.9 mm thick. This electrode was suspended in a laboratory cell flooded with 9M KOH and discharged against an anode while its potential was measured against a zinc reference electrode. Discharge current was 100 mA/g-EMD and was supplied by a computerized battery test unit.

Analytical Characterization of EMD Samples: The following physical, chemical and electrochemical properties of each EMD sample were determined: BET surface area, pore volume, pore-size distribution, compressed density, open-circuit

voltage in 9M KOH solution, and intrinsic discharge capacity. Additionally, many of the samples were X-rayed using the powder diffractometer method, and some were also analyzed for percent Mn, MnO<sub>2</sub> and + 110°C water (structural water). Method descriptions and/or references are given below.

Surface Area, Pore Volume and Pore Size Distribution:

The samples were outgassed at 150°C for 7 hr. in vacuum, and then the sorption measurements were made with a Quantachrome Autosorb 6 instrument using Quantachrome software Autosorb for Windows, Version 1.1. Total pore volume (cm<sup>3</sup>/kg) was determined from the nitrogen adsorbed as the pressure increased from vacuum to 99.6% of atmospheric pressure, which corresponded to a maximum pore diameter of ~4500 Å. Pore volumes were also calculated over three ranges of pore diameter, i.e., 12-30 Å, 30-42 Å and 42-400 Å.

Compressed Density: A cathode mix consisting of 83% dried EMD, 11% KS-44 graphite (Lonza) and 6% 7.2M KOH was compacted into a cylindrical pellet between punches in a one-inch-diameter die. After compaction at 10,000 lb. force, the thickness of the pellet center was measured with a micrometer and the density of the pellet was calculated. The test was conducted in triplicate on each sample, and the results averaged.

Initial Open Circuit Voltage and Intrinsic Discharge

Capacity: A cylindrical laboratory cell was assembled from a cathode of 22% EMD, 65% graphite (KS-44 by Lonza) and 13% 9M KOH, and an anode of zinc wire with a separator between.

5 Cathode mix containing 1.000g EMD (at 1.6% moisture) was pressed into a cylindrical shape onto the steel base of the cell, which also acted as current collector. The cell was flooded with 9M KOH, and the zinc anode was added, the quantity of zinc being much greater stoichiometrically than the EMD. After the open-circuit voltage stabilized (at the initial open circuit voltage, IOCV), the cell was discharged at a constant current of 20 mA per gram of EMD. The intrinsic discharge capacity (in mAh/g-EMD) was determined as the capacity to a cutoff voltage of 1.000V.

10 15 Three cells were assembled from each sample as well as from an EMD sample used as an internal standard with each batch of cells. Therefore, all IOCV's and intrinsic capacities are means of the triplicate tests and are referenced to the internal standard tested at the same time. The method is detailed in the following reference: S.F. Burkhardt, in *Handbook of Manganese Dioxides, Battery Grade*, ed. by D. Glover, B. Schumm, Jr., and A. Kozawa, IBA, Inc., Cleveland, Ohio, 1989, pp. 217-236.

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25 X-ray Diffraction (Q-Ratio): An XRD scan was made of each sample using a Siemens D-500 X-ray diffractometer with

5 CuK $\alpha_1$  radiation and high resolution techniques. Scan rates ranged from 0.1 to 0.6 degrees 20 per minute. Peak heights, corrected for background, were determined at  $2\theta \approx 22^\circ$  and  $37^\circ$ , which are the predominant  $\gamma$ -MnO<sub>2</sub> and  $\epsilon$ -MnO<sub>2</sub> peaks, respectively. The ratio of these peak heights ( $22^\circ/37^\circ$ ) was determined as the Q-ratio. Results were found to be independent of scan rate.

10 Percent Structural Water or +110°C Water: The samples were first dried overnight at 110°C. Then the water driven from the sample at 750°C was determined by means of a Karl Fischer titrator. Each sample was analyzed in triplicate, the individual determinations being conducted on different days.

15 Percent MnO<sub>2</sub> and Mn: The MnO<sub>2</sub> was determined titrimetrically using FeSO<sub>4</sub>. First, an EMD sample is dissolved in an excess of standard acidic FeSO<sub>4</sub> solution to form Mn<sup>2+</sup> ions. Then, the excess Fe<sup>2+</sup> ions are back-titrated with standard permanganate (KMnO<sub>4</sub>) solution. This method assumes that all oxidative power of the EMD is due to Mn(IV) or MnO<sub>2</sub>. Total Mn was determined by first dissolving EMD with a Fe<sup>2+</sup> ion solution and then titrating the resultant Mn<sup>2+</sup> ions in neutral pyrophosphate solution with standard permanganate solution. In this titration the Mn<sup>2+</sup> ions are titrated exactly to Mn<sup>3+</sup> ions. Each sample was analyzed in triplicate, the individual determinations being

conducted on different days. Reference: *Handbook of Manganese Dioxides, Battery Grade*, ed. by D. Glover, B. Schumm, Jr., and A. Kozawa, IBA, Inc., Cleveland, Ohio. 1989, pp. 28-38.

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Test Results

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Table II below lists the EMD samples (first column) along with the deposition parameters (2<sup>nd</sup> through 5<sup>th</sup> columns), relative AA-cell 1-watt discharge energies (6<sup>th</sup> column), and the physical, electrochemical and chemical properties of each (the remaining columns). The table is arranged in order of increasing BET surface area of the EMD (top-to-bottom). The sample used as the comparison standard in AA-cell tests was No. 41.

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Two samples, Nos. 2 and 7, were deposited in a so-called slurry cell, in which manganese oxide particulates were suspended in the deposition bath. In such type of deposition, the EMD surface is much rougher than normal, making the real current density much less than the geometrical or apparent current density. The reason for including samples 2 and 7 in the table was to provide an ample data base for samples with very high compressed density. This will be made apparent in some of the examples below.

TABLE II  
Summary of Samples, Deposition Conditions and Performance Characteristics

EMD #	Deposition Conditions			BET Surface Area (m <sup>2</sup> /g)	Compressed Density (g/cm <sup>3</sup> )	IOCV (V vs. Zn) (mAh/g)	Intrinsic Discharge Capacity (mAh/g)	Q Ratio (%)	Structural H <sub>2</sub> O (%)	Mn (%)	MnO <sub>2</sub> (%)	Pore Volume (cc/g)	Ang. Pore Volume (cc/kg)	Ang. Pore Volume (cc/kg)	42 to 400 (cc/kg)	
	Current Density (A/cm <sup>2</sup> )	Deposition Temp (°C)	Acid Conc (g/l)													
1	0.5	95	30	65.3	8.2	3.24	1.557	2016	2.00	61.4	94.7	0.024	0.6	4.6	9.6	
2	12.0*	95*	30*	74.9	9.7	3.29	1.585	222.9	0.629	2.72	93.4	0.025	1.4	3.9	6.9	
3	1.0	95	30	73.7	13.9	3.22	1.577	234.2	0.855	2.75	60.9	91.9	0.023	1.9	6.6	
4	3.4	97	12	9	100.1	16.7	3.22	1.598	232.0	0.548	-	-	0.028	3.1	7.6	
5	3.4	97	30	115.7	17.0	3.19	1.632	253.1	-	-	-	0.022	5.4	6.6	9.8	
6	3.0	95	31	29	108.9	18.9	3.14	1.610	252.4	0.730	3.25	60.2	91.7	0.024	3.1	
7	9.0*	95*	30*	33*	89.3	19.5	3.23	1.599	239.0	0.949	3.37	92.7	0.026	4.2	6.6	
8	3.4	97	19	15	105.2	19.6	3.19	1.605	244.2	-	-	-	0.028	4.0	7.7	
9	3.4	97	19	5	103.0	20.5	3.20	1.644	256.3	0.500	-	-	0.024	4.7	6.4	
10	4.0	96	14	28	91.6	20.8	3.15	1.583	227.6	0.395	2.76	60.7	92.1	0.034	3.8	10.5
11	3.4	96	26	10	109.6	21.2	3.18	1.632	250.3	-	-	-	0.028	5.7	6.5	
12	3.4	97	30	9	114.4	21.7	3.18	1.646	257.4	-	-	-	0.024	5.3	6.3	
13	3.4	96	29	9	110.7	22.1	3.18	1.642	257.7	-	-	-	0.037	5.5	6.1	
14	3.0	95	31	10	109.8	22.2	3.11	1.612	255.8	0.500	-	-	0.025	5.1	2.4	
15	2.5	96	25	11	115.9	22.4	3.16	1.626	253.3	0.659	3.22	60.4	91.8	0.024	5.3	6.3
16	3.4	96	29	9	115.2	22.4	3.22	1.641	256.1	0.626	3.32	60.1	92.0	0.024	5.8	6.6
17	3.4	96	37	30	98.0	23.0	3.16	1.613	248.4	-	-	-	0.029	5.5	7.9	
18	3.0	95	30	32	95.6	23.3	3.12	1.608	253.2	-	-	-	0.029	4.6	10.4	
19	3.0	95	30	32	102.0	23.3	3.12	1.608	253.2	0.967	-	-	0.029	4.6	10.4	
20	3.0	95	30	10	111.3	23.8	3.13	1.641	253.8	-	-	-	0.027	4.1	7.1	
21	3.0	96	30	10	108.9	24.1	-	253.8	0.547	-	-	-	0.030	4.2	6.6	
22	4.0	95	30	24	107.5	24.4	3.15	1.625	250.8	-	-	-	0.027	4.7	8.4	
23	3.4	96	30	10	111.0	24.9	3.16	1.613	254.6	0.555	-	-	0.032	7.0	8.6	
24	3.0	97	35	10	111.0	25.4	3.17	1.639	254.6	-	-	-	0.032	7.8	8.2	
25	4.2	96	29	11	101.0	26.0	3.13	1.634	248.1	-	-	-	0.034	5.4	6.5	
26	5.0	95	20	10	103.4	26.5	3.12	1.636	253.2	-	-	-	0.031	5.2	9.0	
27	3.4	97	56	21	108.0	27.0	3.13	1.634	251.3	-	-	-	0.032	6.7	8.0	
28	5.0	95	30	19	98.3	27.8	3.06	1.636	252.6	0.8	-	-	0.032	7.0	8.6	
29	6.0	96	36	40	99.3	28.9	3.07	1.603	248.2	-	-	-	0.034	6.1	6.4	
30	5.8	96	37	31	95.9/102.0	29.0	3.09	1.624	248.6	0.6	-	-	0.032	7.6	7.5	
31	3.0	95	70	70	96.4	29.1	3.06	1.619	253.9	-	-	-	-	7.1	12.7	
32	5.8	96	37	31	97.2/105.2	29.6	3.10	1.619	251.4	0.631	3.53	60.6	91.4	0.046	6.5	
33	3.0	95	69	71	101.9	30.0	3.06	1.617	253.4	0.866	3.21	60.1	91.3	0.033	6.0	
34	3.5	97	40	44	96.5	30.1	3.12	1.612	250.6	0.673	3.26	61.7	91.1	0.034	8.4	
35	3.0	95	41	20	107.9	30.4	3.12	1.643	255.0	-	-	-	0.030	5.9	11.8	
36	5.8	96	37	31	104.0	30.9	3.10	1.619	252.5	-	-	-	0.048	7.1	14.3	
37	5.0	95	41	41	98.8	31.8	3.06	1.629	252.4	-	-	-	0.036	8.4	12.1	
38	5.8	96	37	31	100.0	31.8	3.08	1.619	251.7	-	-	-	0.049	7.3	7.5	
39	5.8	96	37	31	103.0	32.1	3.08	1.619	251.4	-	-	-	0.047	7.6	13.6	
40	3.0	95	61	20	98.2	33.5	3.09	1.649	250.6	0.538	-	-	0.034	7.6	8.8	
41	5.8	95	37	31	100.0	33.6	3.07	1.617	250.4	0.602	3.37	60.6	90.7	0.048	7.3	
42	5.8	95	44	27	94.2	33.9	3.10	1.634	250.3	-	-	-	0.038	9.0	10.5	
43	6.0	95	20	13	94.5	34.1	3.07	1.631	250.2	0.430	-	-	0.039	8.3	10.2	
44	5.8	95	49	24	91.8	34.1	3.11	1.633	249.2	-	-	-	0.035	8.9	10.8	
45	5.0	97	41	10	103.4	34.9	3.11	1.643	251.0	-	-	-	0.035	8.6	9.5	
46	5.8	97	36	32	94.9	35.6	3.08	1.626	250.4	-	-	-	0.036	9.6	12.2	

\* Slurry cells

TABLE II (cont'd.)

EMD Sample #	Deposition Conditions			1-Watt Discharge Energy (% base)	BET Surface Area (m²/g)	Compressed Density (g/cm³)	ICCV (V vs. Zn) Discharge Capacity (mAh/g)	Q Ratio H₂O (%)	Structural H₂O (%)	Mn (%)	MnO₂ (%)	Pore Volume (cc/g)	12 to 30 Ang. Pore Volume (cc/kg)	30 to 42 Ang. Pore Volume (cc/kg)	42 to 400 Ang. Pore Volume (cc/kg)
	Current Density (A/I²)	Deposition Temp (°C)	Acid Conc (g/l)												
47	5.8	95	37	30	97.7	35.9	3.09	1.627	248.1	-	-	0.040	9.7	11.5	9.4
48	5.8	95	49	24	101.2	36.1	3.11	1.633	249.2	0.585	-	0.035	8.9	9.9	8.0
49	7.5	95	18	31	94.9	36.3	2.98	1.611	243.3	0.559	-	0.043	8.0	17.3	11.6
50	5.8	95	48	26	94.1	37.2	3.09	1.634	249.6	-	-	0.042	10.1	10.8	9.8
51	7.5	95	19	71	91.1	37.5	2.94	1.606	242.6	-	-	0.043	7.9	14.7	12.9
52	6.0	95	30	91	101.6	40.6	3.05	1.609	245.7	-	-	0.042	9.4	15.4	8.5
53	7.5	95	20	71	96.0	41.2	2.94	1.605	243.4	0.488	-	0.044	8.5	19.6	8.6
54	5.8	97	39	11	94.9	43.7	3.05	1.645	248.6	0.408	3.60/3.72	59.9	91.1	10.5	12.0
55	6.0	95	52	71	86.3	45.3	3.04	1.628	245.7	0.537	-	0.042	12.5	12.8	8.0
56	9.0	95	22	52	77.9	45.5	3.01	1.600	241.4	0.425	-	0.052	9.3	21.2	14.2
57	7.5	93	92.6	7.5	84.4	45.7	2.95	1.608	243.7	0.447	3.53	60.4	90.2	0.061	8.2
58	7.5	93	92.6	7.5	87.6	46.9	2.95	1.608	243.7	0.451	-	-	0.064	8.5	22.7
59	5.8	97	69	70	96.0	52.0	-	1.600	236.3	-	-	0.047	13.8	13.6	13.0
60	7.5	84	84	7.5	60.0	86.4	2.56	1.577	216.2	-	-	0.010	17.7	40.1	37.8
61	7.5	83	83	7.5	51.6	97.2	2.58	1.576	214.2	-	-	-	21.0	35.0	34.8

### Slurry cells

In order to further illustrate the EMD and methods of the present invention, the following examples are given. In the examples,  $i$ =current density,  $T$ =temperature,  $[H_2SO_4]$ =concentration of sulfuric acid and  $[Mn^{2+}]$ =concentration of  $Mn^{2+}$  ions.

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#### Example 1

The materials described in the examples of the invention were as good as or better than any other materials tested. In particular, the best materials were deposited at the following conditions:  $i=2.5-3.5 A/ft^2$ ,  $[H_2SO_4] \approx 30 g/l$  and  $[Mn^{2+}] \approx 10 g/l$ . From visual inspection, Table II indicates that at  $i < 2.5 A/ft^2$  (the top entries in the table), and at  $i > 6 A/ft^2$  and/or  $T < 95^\circ C$ , the product EMD produces a substantially lower discharge energy than at the optimum deposition  $i$  and  $T$ . For the samples deposited at current densities from 2.5 to 6.0  $A/ft^2$ , for which there are numerous samples and significant scatter in the results, a multiple regression was performed of the AA-cell energies vs. the four deposition parameters to de-couple the effects of deposition parameters and the random error in the discharge energies. In this regression, the results for the "standard" sample, No. 41, were given a weight of 20 because this sample was discharged on more than 20 occasions (every week), whereas the other samples were

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generally discharged on just one occasion. Results of this regression are given by the following expression.

Relative discharge energy at rate of 1 Watt =

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$$-2.327 - 1.686i + 0.770T + 3.685[H_2SO_4] - 0.0906[H_2SO_4]^2 + 0.00067[H_2SO_4]^3 - 0.345[Mn^{2+}] + 0.00274[Mn^{2+}]^2 \quad (\text{Eq.1})$$

This expression yielded a correlation coefficient,  $R$ , of 0.794, which indicates a nominally good fit of the data. Several other expressions with respect to the independent variables gave approximately equally good, but no better, correlation coefficient than the above expression. These expressions generally showed the same effects of the parameters. Thus, it appears that the limitations in fitting the data are more because of limitations in the precision of the data than of the misfit between the regression and the experimental energies.

The statistical significance of fitting the various coefficients in Eq. (1) is very high (>98%) except in the case of temperature. Here the significance of fit to the coefficient is only 73%. The significant effects of the deposition parameters are indicated by the coefficients, as follows. The effect of temperature is to increase the discharge energy by 0.77% per degree C. The effect of current density is to decrease the discharge energy by 1.69% for each A/ft<sup>2</sup>. This is shown in FIG. 1 at chosen electrolyte conditions of T=95°C, [H<sub>2</sub>SO<sub>4</sub>]=30 g/l, and [Mn<sup>2+</sup>]=30 g/l. One observes that decreasing  $i$  from 6.0 A/ft<sup>2</sup> to

2.5 A/ft<sup>2</sup> increases the discharge energy by almost 6%. FIG. 1 does not show  $i$  values less than 2.5 A/ft<sup>2</sup>. Since the discharge energy drops rapidly between 2.5 and 1.0 A/ft<sup>2</sup> (Table II), this area was not investigated in detail.

5 FIG. 2 shows the results of Eq. 1 in topographical form for fixed  $i$  and  $T$ , and variable  $[H_2SO_4]$  and  $[Mn^{2+}]$ . Lines are drawn for equal energy intervals of 3% between 91 and 112%. The best energies are observed near 30 g/l  $H_2SO_4$  and 5 g/l  $Mn^{2+}$ . The energy then decreases as either  $[H_2SO_4]$  or  $[Mn^{2+}]$  is increased. The energy then increases slightly again at  $[H_2SO_4] > 60-65$  g/l. These and higher  $H_2SO_4$  concentrations are not desired, because they foster passivation of the bare titanium anodes, which raises the cell voltage during deposition and can cause cell shutdown.

10 15 A significant finding is that the discharge energy is defined by not only the acid and  $Mn^{2+}$  concentrations but also the ratio  $[H_2SO_4] / [Mn^{2+}]$ , as evidenced from the shapes of the contour lines.

20 From Eq. (1) and FIG. 1 and 2 one could define deposition parameters that produce excellent product (arbitrarily chosen as >108% of the energy for the internal standard) and good (arbitrarily chosen as 100-108% of the energy for the internal standard). These conditions are approximately:

Excellent Deposition Conditions:

$i=2.5-3.5 \text{ A/ft}^2$ ;  $T=95-98^\circ\text{C}$ ;  $[\text{H}_2\text{SO}_4]=25-40 \text{ g/l}$ ;  $[\text{Mn}^{2+}]=5-20 \text{ g/l}$ .

Deposition Conditions Good:

5  $i=3.6-6.0 \text{ A/ft}^2$ ;  $T=95-98^\circ\text{C}$ ;  $[\text{H}_2\text{SO}_4]=41-50 \text{ g/l}$ ;  $[\text{Mn}^{2+}]=21-50 \text{ g/l}$ .

**Example 2**

Example 2 shows that the inventive EMD has superior high-drain battery performance to and also different properties than EMD deposited at prior art conditions. "Prior art EMD's" were taken as all those in Table II for which the deposition current density was 5.8 or 6.0  $\text{A/ft}^2$  (18 in number). For the present invention, we use all the samples in Table II that were deposited under the most preferred conditions as defined in Example 1, i.e., 2.5-3.5  $\text{A/ft}^2$ , 95-98 $^\circ\text{C}$ , 25-40 g/l  $\text{H}_2\text{SO}_4$  and 5-20 g/l  $\text{Mn}^{2+}$ . This includes Samples 5, 11-16, 20, 21, 23, 24 and 35 (12 in number). The performances and properties of all the samples within each group were averaged to represent the group. Comparison of the inventive EMD's and the prior art EMD's are shown in Table III below in terms of the mean performance features or properties and the standard deviations for the individual values about the means. Several entries in Table III are those shown in Table I.

25 The inventive EMD's are statistically different from the prior art EMD's in most respects. In several cases the

difference in property directly relates to obvious superiority in application, i.e., the higher 1-watt discharge capacity and energy translate into longer running time in high-rate applications; the higher intrinsic discharge capacity ensures a greater capacity at lower-rate applications; the greater initial open circuit voltage is valued by battery makers (and is part of the reason for the greater capacities); and greater compressed density translates into more material being placed in each cell.

The other differences largely verify and define differences in structure, and provide the means by which EMD discharge rates differ. The pores, defined by the BET surface area, the pore volume and the pore volume distribution, are the dislocations and interstitial spaces between solid crystallites and aggregates of crystallites. The prior art EMD's have more such space than the inventive EMD's at all levels (sizes) of interstices. This excess space interferes with proton movement through the EMD during discharge, the latter proton movement being necessary to sustain the electrochemical discharge reaction, which is given by Eq. (2).



The stoichiometric differences, as represented by %  $\text{MnO}_2$ , Mn and structural water, are smaller than the differences in porosity. Nevertheless, these small differences can contribute to the initial open circuit

voltage and discharge differences, i.e., the Mn oxidation number (being proportional to % MnO<sub>2</sub>/%Mn) favors the inventive EMD slightly, since %MnO<sub>2</sub> is slightly greater for the inventive material.

TABLE III

	EMD of the Present Invention (12 samples)	Prior Art EMD (18 samples)
Deposition Conditions	2.5-3.5 A/ft <sup>2</sup> 95-97°C 15-40 g/l H <sub>2</sub> SO <sub>4</sub> 5-20 g/l Mn <sup>2+</sup>	5.8-6.0 A/ft <sup>2</sup> 95-97°C 20-69 g/l H <sub>2</sub> SO <sub>4</sub> 11-91 g/l Mn <sup>2+</sup>
EMD Properties		
AA-Cell Discharge Capacity at 1 Watt Discharge Rate (mAh/g)	68.2 $\sigma=4.4$	63.4 $\sigma=7.0$
AA-Cell Discharge Energy at 1 Watt Discharge Rate (mWh)	755 $\sigma=19$	637 $\sigma=6.9$
Intrinsic Discharge Capacity (mAh/g)	254.6 $\sigma=2.0$	248.8 $\sigma=3.6$
Initial Open Circuit Voltage (V vs. Zn)	1.639 $\sigma=0.006$	1.623 $\sigma=0.012$
Compressed Density (g/cm <sup>3</sup> )	3.162 $\sigma=0.035$	3.080 $\sigma=0.021$
% MnO <sub>2</sub>	91.9 $\sigma=0.1$	91.1 $\sigma=0.3$
% Mn	60.1 $\sigma=0.3$	60.4 $\sigma=0.4$
% Structural H <sub>2</sub> O	3.28 $\sigma=0.05$	3.52 $\sigma=0.15$
BET Surface Area (m <sup>2</sup> /g)	23.5 $\sigma=3.2$	34.8 $\sigma=4.6$
Total Pore Volume (cm <sup>3</sup> /kg)	27 $\sigma=4$	41 $\sigma=5$
12-30 Å Pore Volume (cm <sup>3</sup> /kg)	5.4 $\sigma=0.07$	8.9 $\sigma=2.0$
30-42 Å Pore Volume (cm <sup>3</sup> /kg)	6.1 $\sigma=1.2$	12.5 $\sigma=2.1$
42-400 Å Pore Volume (cm <sup>3</sup> /kg)	6.4 $\sigma=1.3$	9.3 $\sigma=1.7$
XRD Q-Ratio	0.58 $\sigma=0.06$	0.54 $\sigma=0.09$

**Example 3**

FIG. 3 shows the experimental AA-cell discharge energies vs. the BET surface areas for all the samples of Table I. Vertical lines are drawn to define a surface-area range within which practically all the excellent EMD's lie (excellent EMD's being arbitrarily defined as earlier, i.e., those yielding AA-cell energies equal to or greater than 108% of Sample 41). All such EMD's were deposited according to the preferred method of the invention. It is observed that the range of excellence does not screen out all sub-excellent materials. Rather, this range is meant to indicate whether or not a material has a high probability of being sub-excellent, by virtue of its surface area lying outside the range of excellence. The range of excellence is approximately  $21-29 \text{ m}^2/\text{g}$ . This range excludes one sample in FIG. 3 with a surface area of  $17 \text{ m}^2/\text{g}$  and a discharge energy  $> 108\%$ . However, many other samples with surface areas in the range of  $17-21 \text{ m}^2/\text{g}$  yield discharge energies less than 108%. Surface areas greater than the range of excellence are dominated by EMD's deposited by prior art of higher current densities than preferred (i.e.,  $i > 5 \text{ A}/\text{ft}^2$ ) and lower temperatures than preferred (i.e.,  $T < 95^\circ\text{C}$ ). Surface areas less than the range of excellence contain EMD's deposited at current densities less than the inventive method (i.e.,  $< 2 \text{ A}/\text{ft}^2$ ), EMD's

deposited from electrolyte with non-preferred acid and/or manganese concentrations, or EMD's deposited from a slurry cell.

**Example 4**

5 FIG. 4 shows the experimental AA-cell discharge energies as a function the compressed density for all the samples of Table I. The range of excellence, defined as in Example 3, includes compressed densities between approximately 3.09 and 3.21 g/cm<sup>3</sup>. Compressed densities below the range of excellence are dominated by the same EMD's that possess surface areas that are too high (FIG. 3); these were deposited by prior art of higher current densities and/or lower temperatures than preferred. Compressed densities greater than the range of excellence 10 contain the same EMD's that were outside the range of excellence on the low-surface-area side, as detailed in Example 3.

**Example 5**

20 FIGS. 5 and 6 show the experimental AA-cell discharge energies as functions of the initial open circuit voltages (IOCV's) and intrinsic discharge capacities, respectively, for all the samples of Table I. In these cases the range of excellence starts at approximately 1.62 V (IOCV) or 250 mAh/g (intrinsic capacity) and is unbounded on the high 25 end. The results indicate that samples have little chance

of excellence at high drain if their IOCV or intrinsic discharge capacity is less than that of Sample 41 (open circle).

#### Example 6

5        The X-ray diffraction (XRD) spectrum for a typical, good EMD is shown in FIG. 10. All the peaks in this spectrum are characteristic of EMD's and have been indexed as representing the continuous crystallographic series between the  $\gamma$ -MnO<sub>2</sub> and  $\epsilon$ -MnO<sub>2</sub> phases. All the members of this series are often collectively termed  $\gamma$ - $\epsilon$  MnO<sub>2</sub>. The crystallography of such EMD's may be defined further in terms of the  $\gamma$ -MnO<sub>2</sub>/ $\epsilon$ -MnO<sub>2</sub> character of the EMD, defined as the relative peak heights of the 22° and 37° peaks (after correction for background). This ratio of peak heights, 10      22°/37°, termed the "Q-ratio" is shown in FIG. 7 vs. the experimental AA-cell 1-watt discharge energies for a representative number of the samples. Q-ratios lie between about 0.47 and 0.76 for excellent EMD's. This range also happens to include some prior art EMD's, including Sample 15      41. EMD's with too high of a Q-ratio were deposited at very low current densities or from a suspension bath. In addition to appropriate Q-ratios, the excellent and good EMD's must show clean  $\gamma$ / $\epsilon$ -MnO<sub>2</sub> patterns as shown in FIG. 10, and not show detrimental phases. FIG. 11, for Sample No. 20      4, exhibits a prominent peak for  $\beta$ -MnO<sub>2</sub> at about 28.8°, even

though its Q-ratio is 0.55, which falls within the range of excellence.  $\beta$ -MnO<sub>2</sub> is a battery-inactive phase in rapid alkaline discharge. Other EMD's deposited from low-acid baths (i.e., <15 g/l H<sub>2</sub>SO<sub>4</sub>) also exhibited the  $\beta$ -MnO<sub>2</sub> peak.

5

#### Example 7

10

FIGS. 8 and 9 show experimental AA-cell discharge energies as a function of the chemical composition for 17 of the 61 test EMD's, the chemical composition being defined by the percentage of structural water (FIG. 8) and MnO<sub>2</sub> (FIG. 9). The range of excellence is approximately 3.17-3.38% structural H<sub>2</sub>O and 91.5-92.1% MnO<sub>2</sub>. Samples that are outside these ranges of excellence because of low structural water content or high MnO<sub>2</sub> content were deposited either at very low current density or in a slurry cell. Samples with structural water contents greater than the range of excellence or MnO<sub>2</sub> contents less than the range of excellence generally were deposited by prior art methods at high current densities ( $\geq 5.8$  A/ft<sup>2</sup>), low temperatures ( $<95^{\circ}\text{C}$ ), or at non-preferred acid and manganese concentrations.

15

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#### Example 8

Table IV below shows the average relative flooded half-cell discharge capacities for 19 of the EMD's described in Table II. Each capacity is the mean of three

or more individual cell capacities. As with the AA-cell energies, the half-cell capacities of Table IV are compared to the mean capacity for Sample 41, which was discharged more than 30 times from several different cathode mixes.

5 The absolute capacity for Sample 41 was 227 mAh/g. Also given in Table IV are the EMD surface areas and the relative rankings of the deposition conditions based on Example 1.

10 One observes excellent correspondence between the relative capacities and the rankings of the deposition conditions. That is to say, the most preferred deposition conditions ( $2.5\text{-}3.5\text{ A/ft}^2$ ,  $25\text{-}40\text{ g/l H}_2\text{SO}_4$  and  $5\text{-}20\text{ g/l Mn}^{2+}$ ) clearly yielded the highest capacities, which were 101-105%; the so-called "good" conditions ( $3.6\text{-}6\text{ A/ft}^2$ ,  $41\text{-}50\text{ g/l H}_2\text{SO}_4$  and  $21\text{-}50\text{ g/l Mn}^{2+}$ ) yielded the next best capacities of 96.0-100.0%; and the poorest conditions, i.e., those outside of both the excellent and good ranges, yielded the poorest capacities, which were between 86 and 94%. The half-cell capacities thus parallel the AA-cell energies with regard to relative performance vs. deposition conditions and EMD properties. These results also complement the AA-cell results, since the half-cell results do not involve anode potentials, and represent constant weight of EMD in each case.

TABLE IV

Half-Cell Results

	EMD Sample	BET Surface Area (m <sup>2</sup> /g)	Half-Cell Discharge Capacity to 0.9V (% base)	Range of Deposition Conditions (per Example 1)
5	1	8.2	86.8	less than good
	4	16.7	88.5	less than good
	8	19.6	93.8	less than good
	9	20.5	99.6	good
	10	20.8	91.5	less than good
10	13	22.1	104.4	excellent
	15	22.4	103.9	excellent
	16	22.4	105*	excellent
	23	24.9	101.4	excellent
	25	26.0	98.2	good
15	28	27.8	97.4	good
	30	29.0	96.9	good
	33	30.0	86.4	less than good
	34	30.1	98.2	good
	36	30.9	96.9	good
20	39	32.1	96.0	good
	41	33.6	100.0	good
	54	43.7	99.6	good
	58	46.9	85.9	less than good

\* 5 sets of tests with different cathode mixes

Thus, the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned as well as those which are inherent therein. While numerous changes may be made by those skilled in the art, such changes are encompassed within the spirit of this invention as defined by the appended claims.

What is claimed is:

PATENT  
Case No. 1060

1. A method of producing EMD having a high discharge capacity at high discharge rates by electrolysis in an electrolytic cell having cathodic and anodic electrodes disposed therein comprising the steps of:

5                    maintaining a heated aqueous electrolyte solution comprising sulfuric acid and manganese sulfate in said electrolytic cell, said solution having manganese sulfate therein in an amount whereby manganese ion is present in the range of from about 5 to about 50 grams of manganese ion per liter of solution; and

10                  applying electric current to said electrodes whereby said anodic electrode current density is in the range of from about 2.5 to about 6 amperes per square foot and said high discharge capacity EMD produced is deposited 15 on said anodic electrode.

2. The method of claim 1 wherein said aqueous solution is maintained in said electrolytic cell at a temperature in the range of from about 95°C to about 98°C.

3. The method of claim 1 wherein said aqueous electrolyte solution has a sulfuric acid concentration therein in an amount in the range of from about 20 to about 60 grams of sulfuric acid per liter of solution.

5 4. The method of claim 1 wherein the amount of sulfuric acid in said electrolyte solution is greater than or equal to two times the amount of manganese ion therein.

5. The method of claim 1 wherein said cathodic electrode is comprised of copper.

10 6. The method of claim 1 wherein said anodic electrode is comprised of titanium.

7. A method of producing EMD having a high discharge capacity at high discharge rates by electrolysis in an electrolytic cell having cathodic and anodic electrodes disposed therein comprising the steps of:

5                    maintaining an aqueous electrolyte solution comprised of sulfuric acid and manganese sulfate in said electrolytic cell at a temperature in the range of from about 95°C to about 98°C, said solution having sulfuric acid therein in an amount in the range of from about 20 to about 10 60 grams of sulfuric acid per liter of solution and having manganese sulfate therein in an amount whereby manganese ion is present in the range of from about 5 to about 50 grams of manganese per liter of solution; and

15                  applying electric current to said electrodes whereby said anodic electrode current density is in the range of from about 2.5 to about 4.5 amperes per square foot and said high discharge capacity EMD produced is deposited on said anodic electrode.

20                  8. The method of claim 7 wherein the amount of sulfuric acid in said electrolyte solution is greater than or equal to two times the amount of manganese ion therein.

9. The method of claim 7 wherein the cathodic electrode is comprised of copper.

10. The method of claim 7 wherein said anodic electrode is comprised of titanium.

11. A method of producing EMD having a high discharge capacity at high discharge rates by electrolysis in an electrolytic cell having cathodic and anodic electrodes disposed therein comprising the steps of:

20 applying electric current to said electrodes whereby said anodic electrode current density is in the range of from about 2.5 to about 3.5 amperes per square foot and said high discharge capacity EMD produced is deposited on said anodic electrode.

12. The method of claim 11 wherein said cathodic electrode is comprised of copper.

13. The method of claim 11 wherein said anodic electrode is comprised of titanium.

5 14. EMD having a high discharge capacity at high discharge rates produced in accordance with the method of claim 1.

10 15. EMD having a high discharge capacity at high discharge rates produced in accordance with the method of claim 7.

16. EMD having a high discharge capacity at high discharge rates produced in accordance with the method of claim 11.

15 17. An improved cathode material comprising EMD having an AA-cell discharge capacity at a 1 watt discharge rate of about 68.2 milliampere hours per gram or higher and an AA-cell discharge energy at a 1 watt discharge rate of about 755 milliwatt hours or higher.

18. An improved cathode material comprising EMD having an intrinsic discharge capacity of about 254.6 milliampere hours per gram or higher.

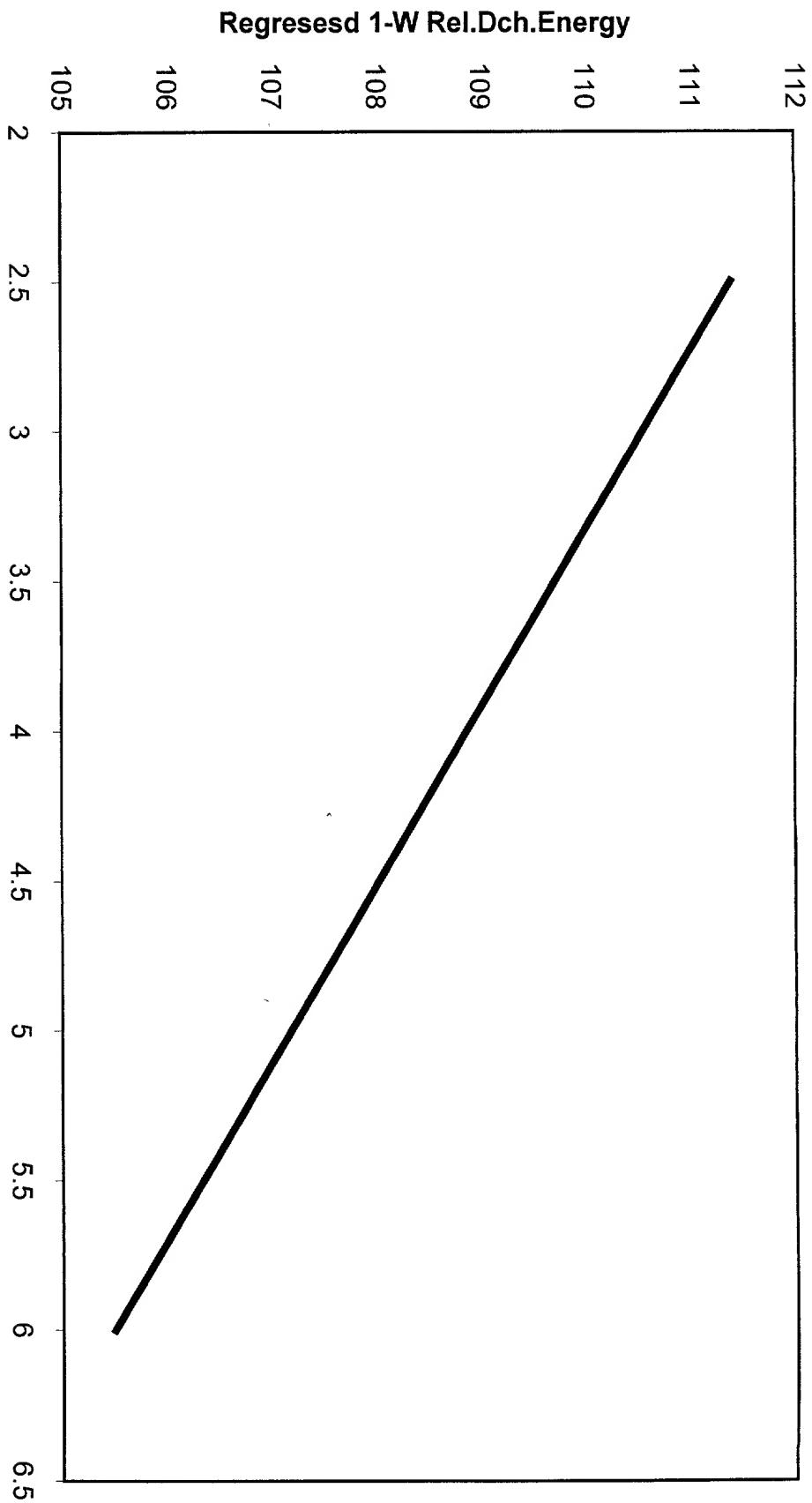
5 19. An improved cathode material comprising EMD having an initial open circuit voltage of about 1.639 volts or higher.

20. An improved cathode material comprising EMD having a compressed density of about 3.162 grams per cubic centimeter or higher.

**Abstract of the Disclosure**

The present invention provides improved cathode material comprised of electrolytic manganese dioxide having high discharge capacity at high discharge rates and methods 5 of producing such electrolytic manganese dioxide by electrolysis in an electrolytic cell. The methods are basically comprised of maintaining a heated high purity aqueous electrolyte solution comprising sulfuric acid and manganese sulfate in the electrolytic cell, the manganese sulfate being present in the solution whereby it contains 10 in the range of from about 5 to about 50 grams of manganese per liter of solution. An electric current is applied to the electrodes of the electrolytic cell whereby the anodic electrode current density is in the range of from about 2.5 to about 6 amperes per square foot. 15

**Fig.1.**



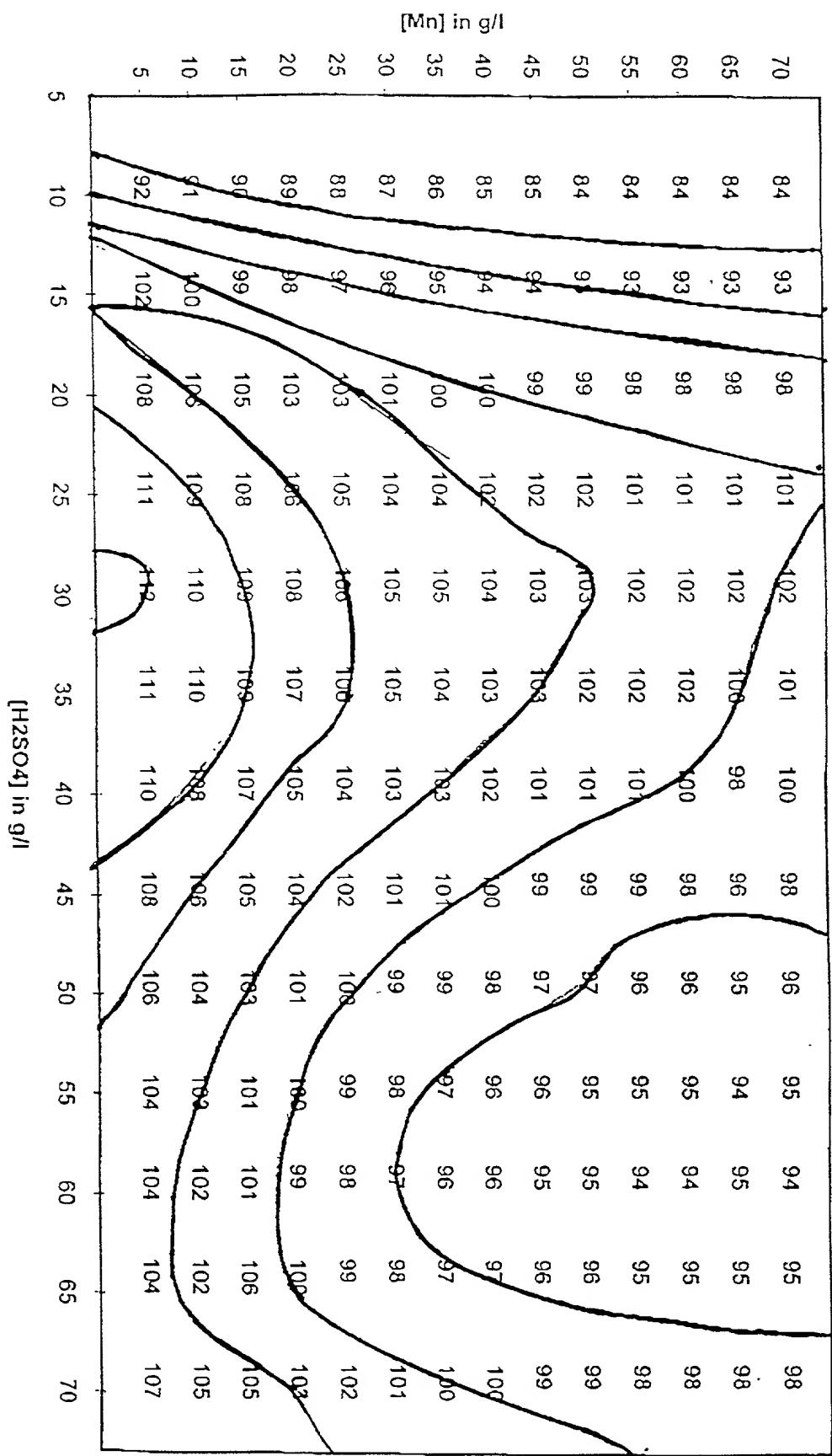


Fig. 2

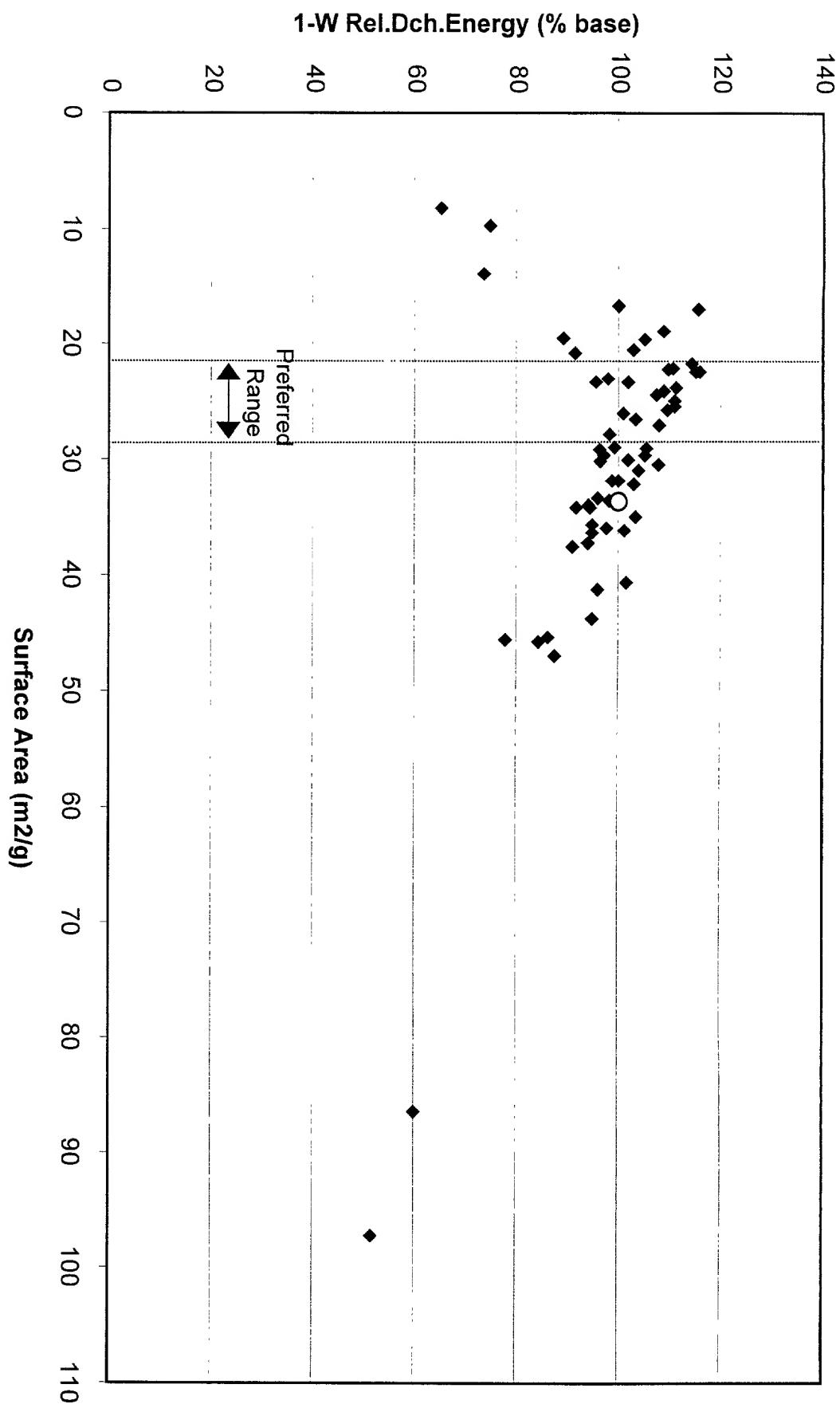


Fig. 3.

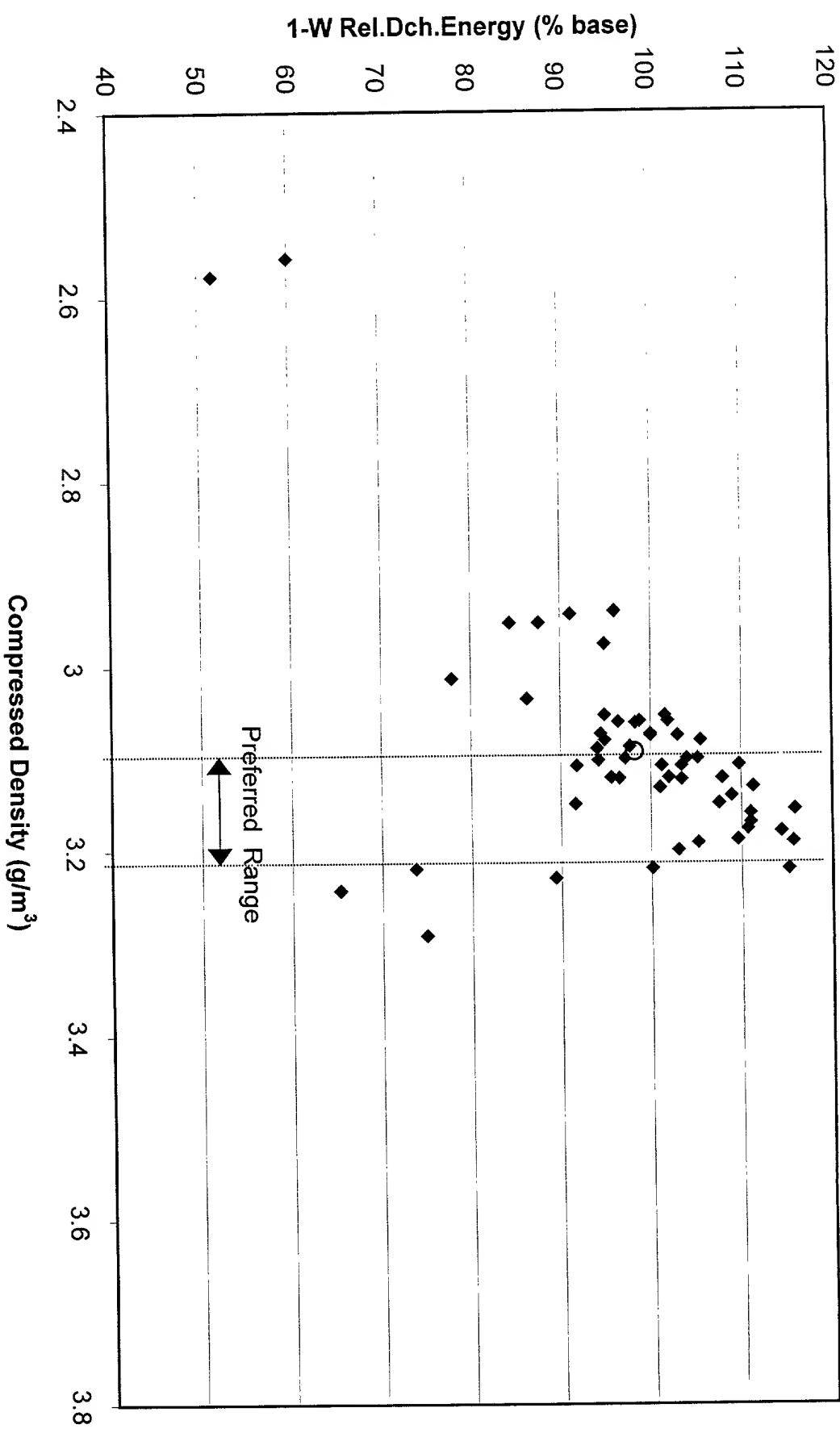


Fig. 4.

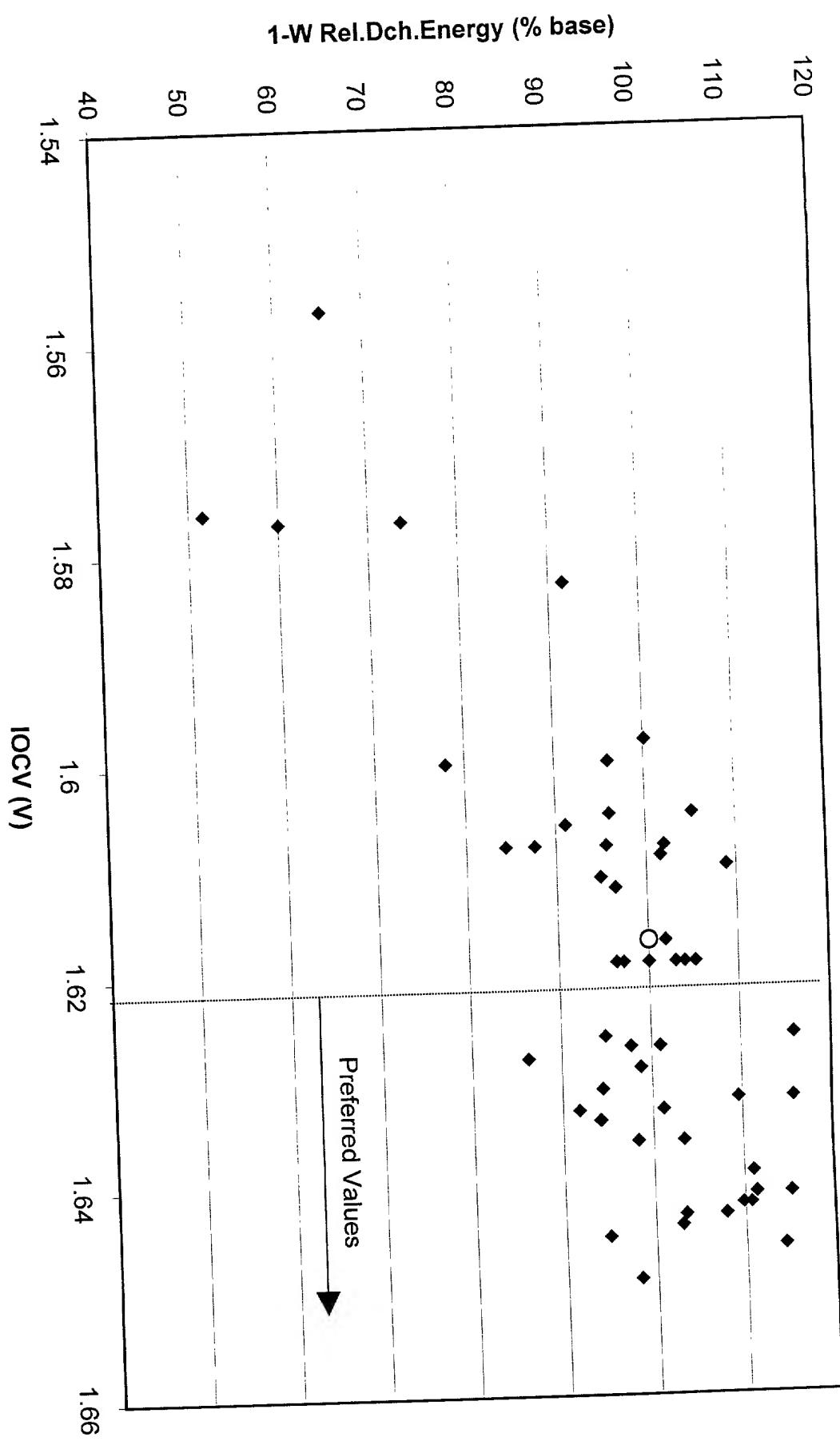


Fig. 5.

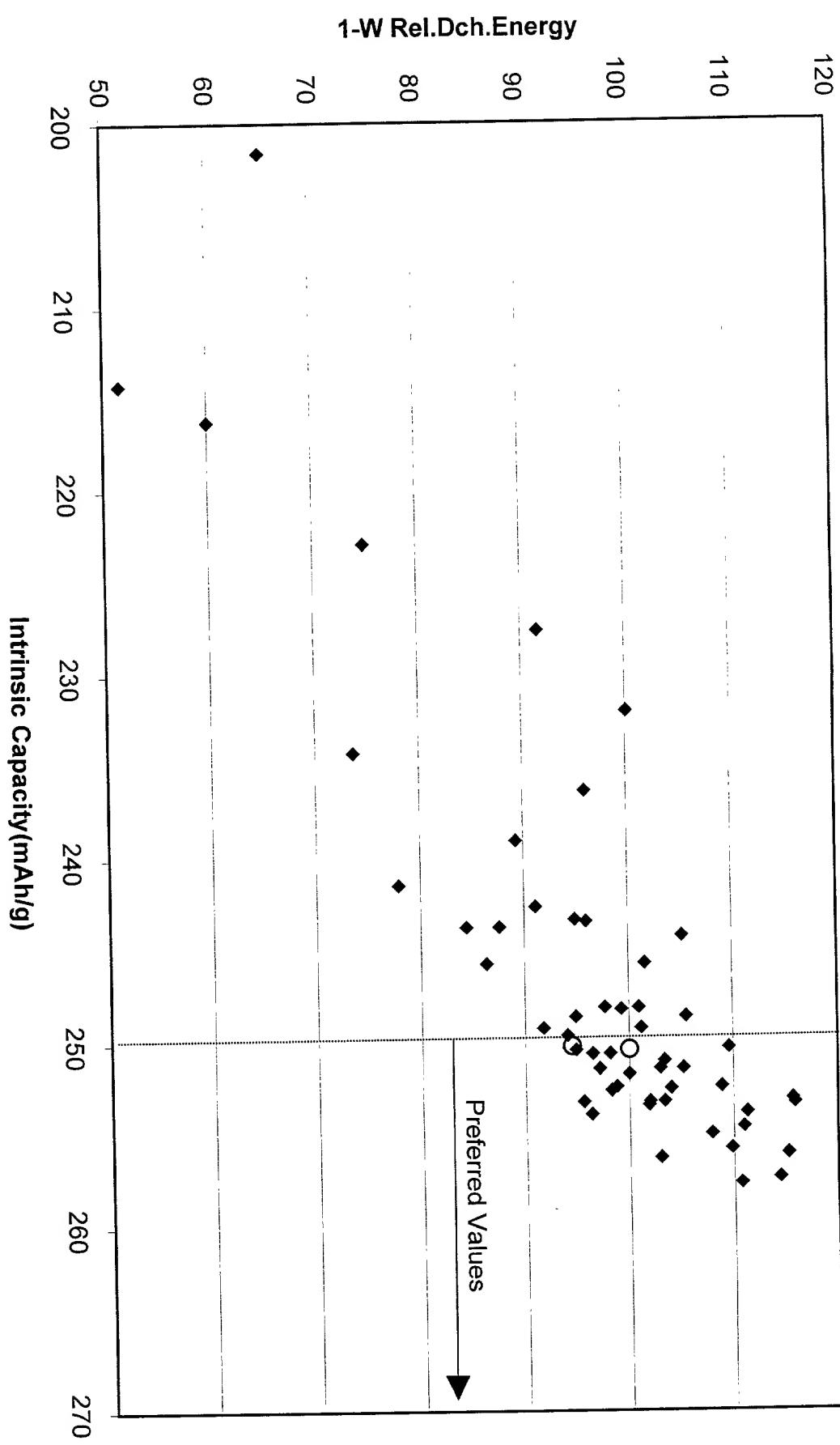


Fig.6.

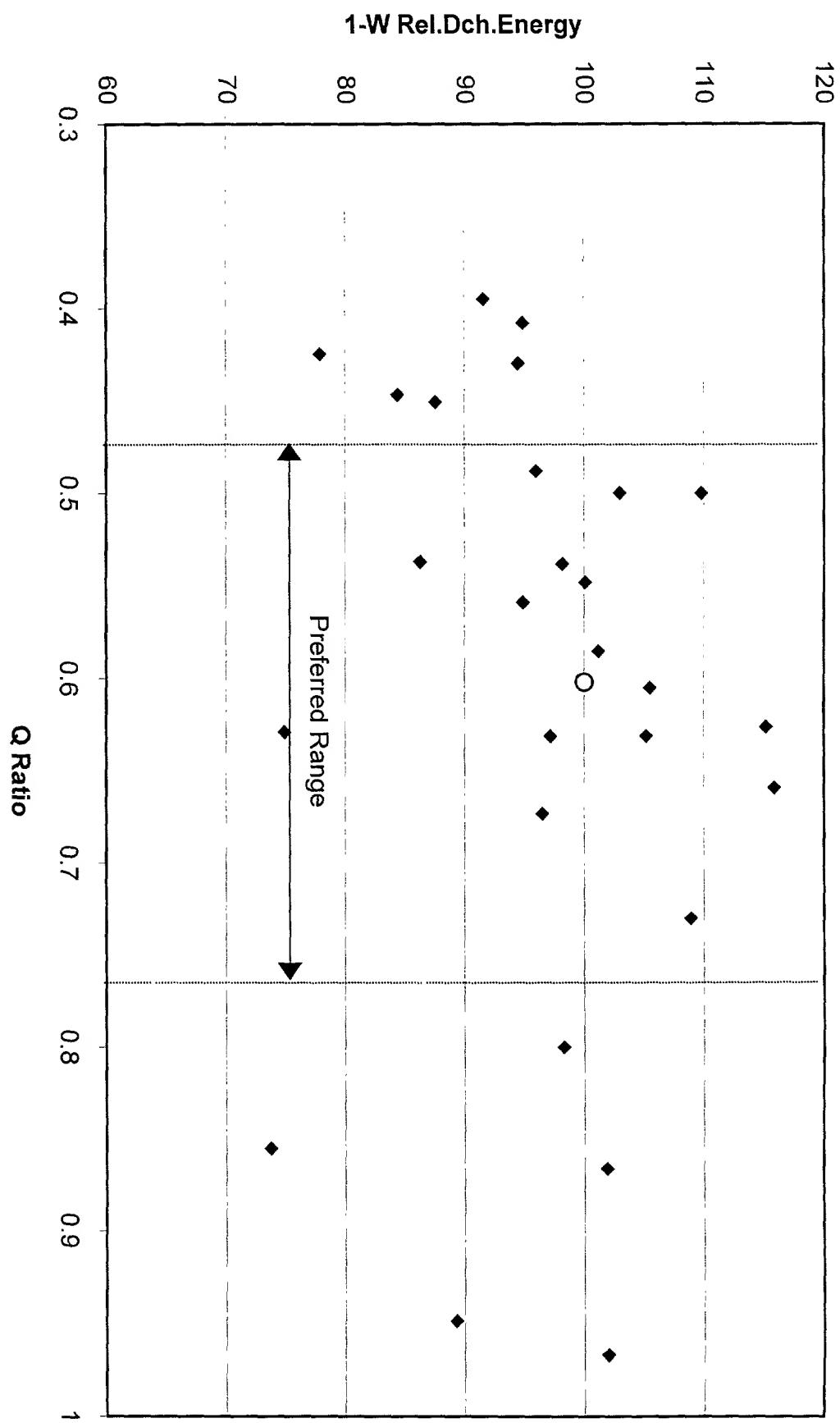


Fig. 7.

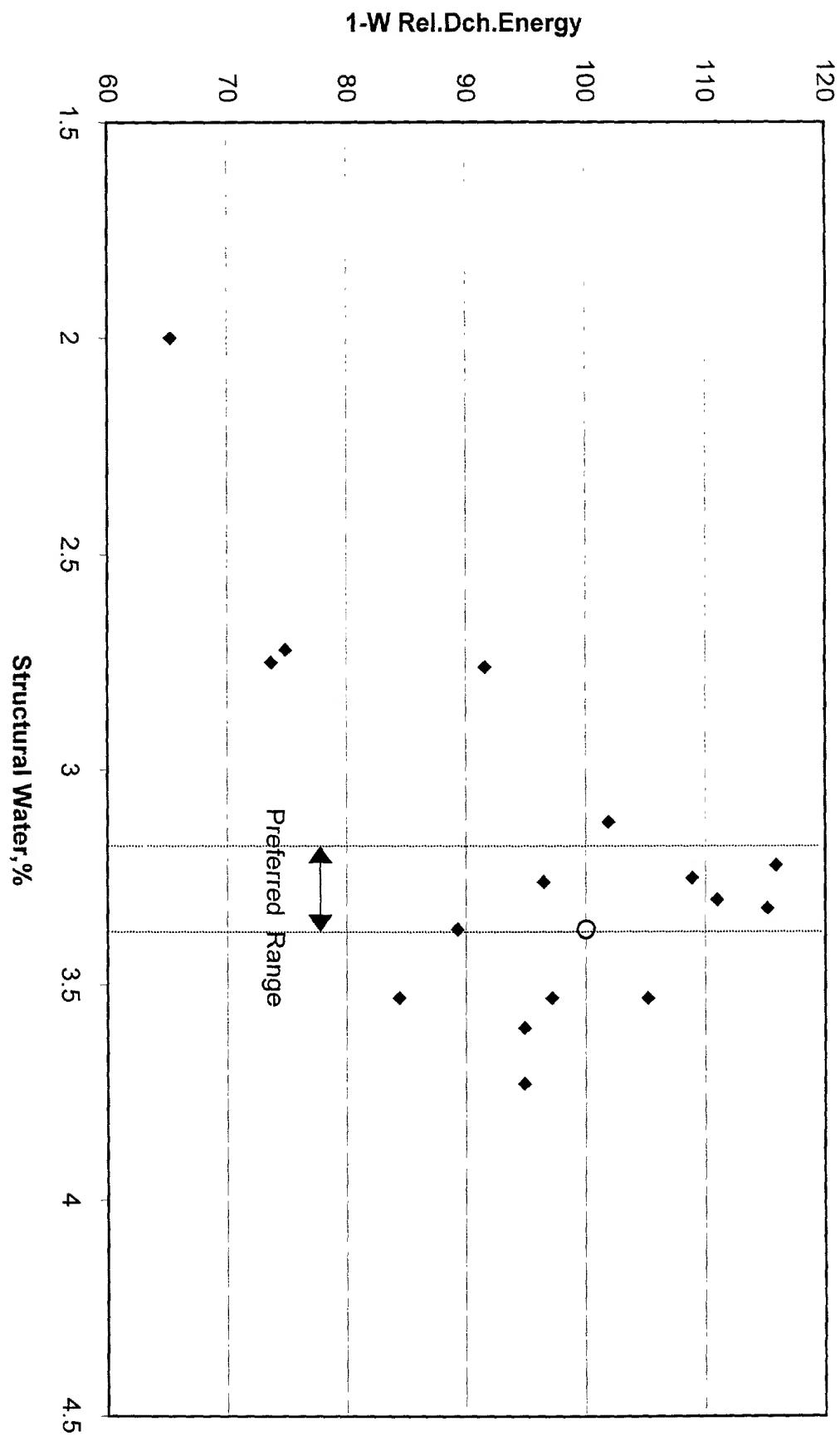


Fig. 8.

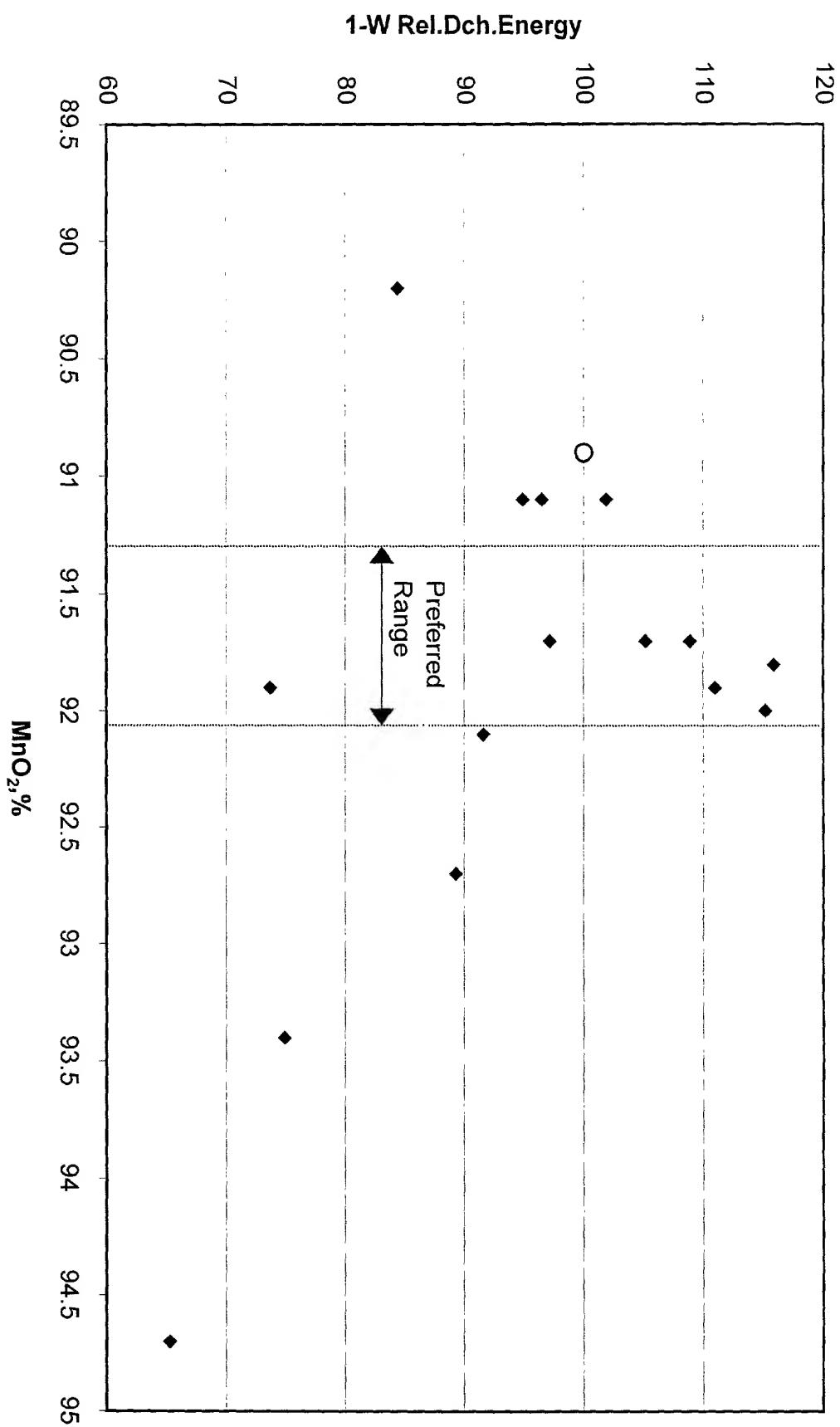


Fig. 9.

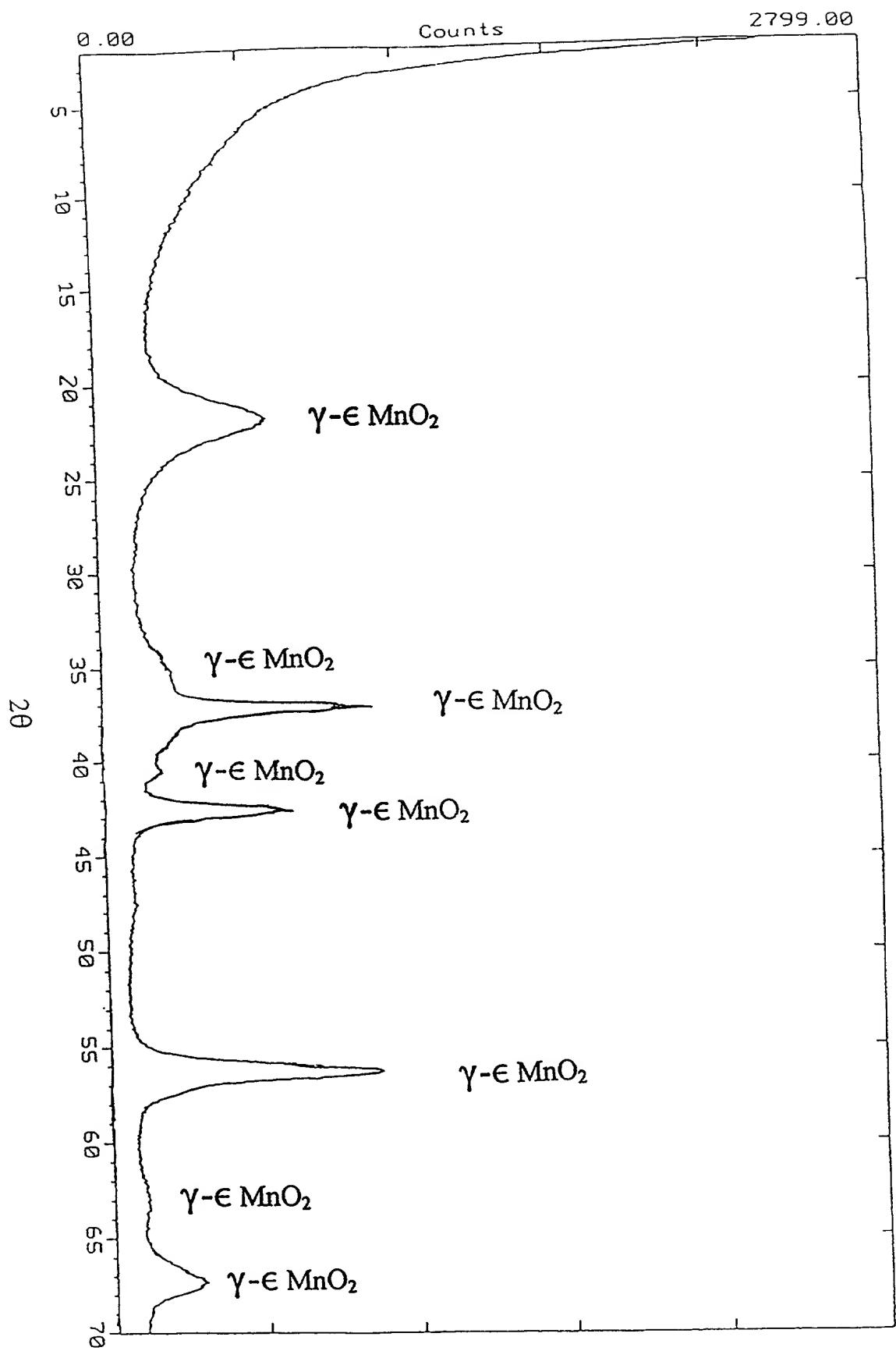
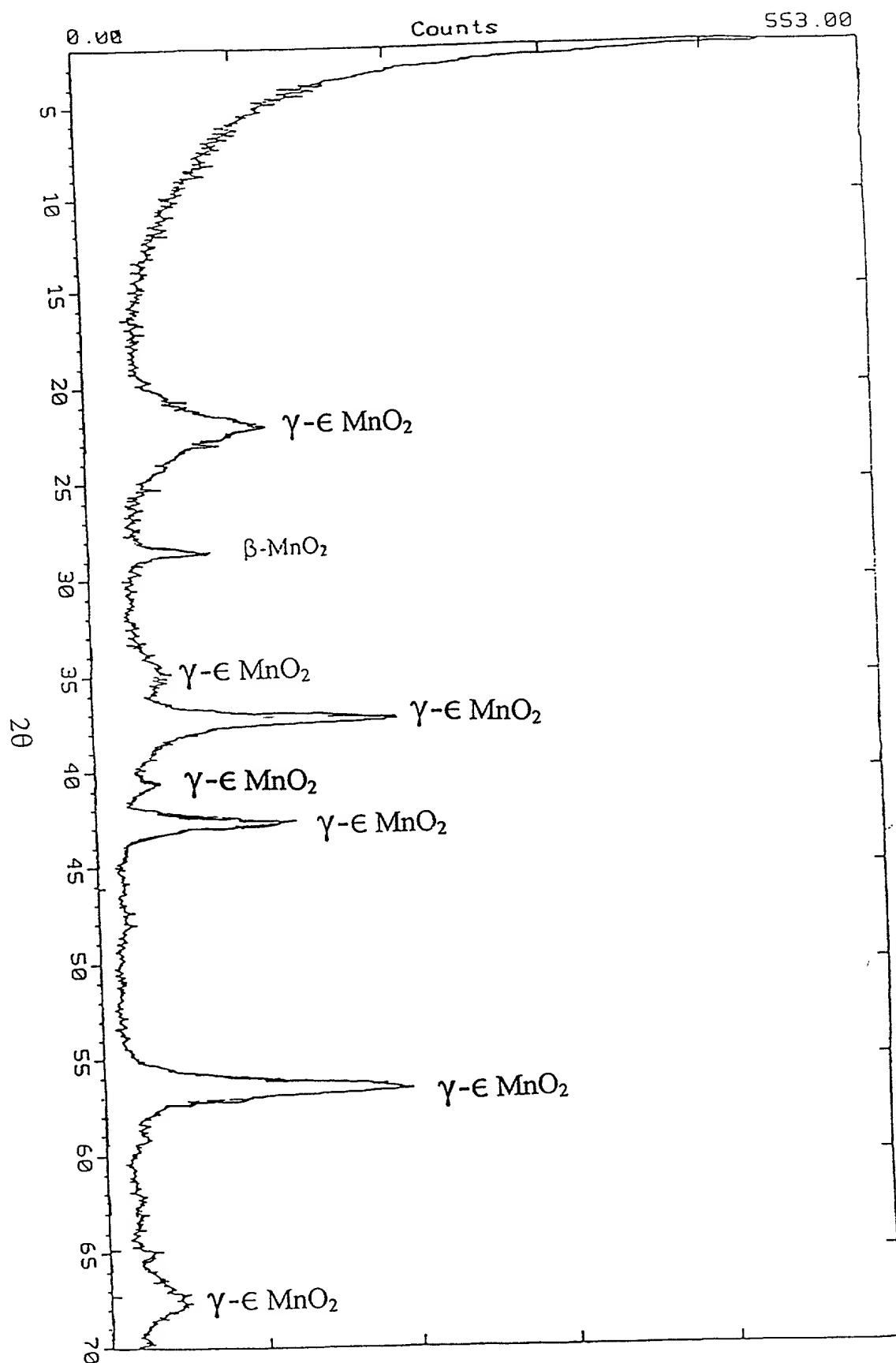


Fig. 10.

Fig. 11.



**SUPPLEMENTAL  
DECLARATION AND POWER OF ATTORNEY**

As a below named inventor(s), I/we hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled **HIGH DISCHARGE CAPACITY ELECTROLYTIC MANGANESE DIOXIDE AND METHODS OF PRODUCING THE SAME**,

the specification of which (check one)

is attached hereto.

was filed on December 21, 1998 as United States Application No. 09/217,168 or PCT International Application No. \_\_\_\_\_ and was amended on \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) or any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below any foreign application for patent or inventor's certificate, or of any PCT international application, having a filing date before that of the application from which priority is claimed:

PRIOR FOREIGN APPLICATION(S)

Priority Claimed

(Number)	(Country)	(Day/month/year filed)
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Yes  No

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s), or 365(c) of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(Status)	(patented, pending, abandoned)
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(Application Serial No.)	(Filing Date)	(Status)	(patented, pending, abandoned)
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I hereby declare that all statement made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As named inventor(s), I/we hereby appoint the following attorneys to prosecute this application and transact all business in the Patent and Trademark Office connected therewith and to receive the Letters Patent Document, if issued.

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